Effects of Acid Rain on Forest Resources

Proceedings of the Conference Held in Sainte-Foy, Quebec
14-17 June, 1983

G. Robitaille and P.J. Rennie, Editors
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Forestry Canada   Forêts Canada

Canada

Forestry Canada

Forestry Canada is the main focus for forestry matters in the federal government. It provides national leadership through the development, coordination, and implementation of federal policies and programs to enhance long-term economic, social, and environmental benefits from the forest sector for Canadians.

Forestry Canada is a decentralized organization with six regions, two national research institutes, and seven regional suboffices located across Canada. Headquarters is located in the National Capital Region in Hull, Quebec.

In support of its mandate, Forestry Canada carries out the following activities:

- administers forest development agreements negotiated with the provinces.
- undertakes and supports research, development, and technology transfer in forest management and utilization.
- compiles, analyzes, and disseminates information about national and international forest resources and related matters.
- monitors disease and insect pests in Canada's forests.
- provides information, analyses, and policy advice on economics, industry, markets, and trade related to the forest sector.
- promotes employment, education, and training opportunities in the forest sector.
- promotes public awareness of all aspects of the forest sector.

Forestry Canada interacts regularly with provincial and territorial governments, industry, labor, universities, conservationists, and the public through such bodies as the Canadian Council of Forest Ministers, the Forest Sector Advisory Council, the Forestry Research Advisory Council of Canada, the Canadian Forest Inventory Committee, the Canadian Committee on Forest Fire Management, the Canadian Interagency Forest Fire Centre, and regional consultative committees. Forestry Canada is also active in international forestry agencies such as the International Union of Forest Research Organizations and the Food and Agriculture Organization, as well as in technical and trade missions.

Forêts Canada

Forêts Canada est l'organisme principal en matière de foresterie à l'intérieur du gouvernement fédéral. Chef de file sur le plan national, il assure la préparation, la coordination et la mise en œuvre des politiques et des programmes fédéraux dans le but d'améliorer les avantages économiques, sociaux et environnementaux à long terme offerts aux Canadiens par le secteur forestier.

Forêts Canada est une organisation décentralisée: six régions, deux instituts de recherche nationaux ainsi que sept sous-bureaux régionaux sont répartis dans tout le Canada. L'administration centrale est établi dans la région de la Capitale nationale, à Hull (Québec).

Pour remplir son mandat, Forêts Canada assume les tâches suivantes:

- Il administre les accords de développement forestier conclus avec les provinces;
- il entreprend et appuie la recherche, la mise au point et le transfert technologique dans le domaine de la gestion et de l'utilisation des forêts;
- il rassemble, analyse et diffuse de l'information sur les ressources forestières nationales et internationales et les domaines connexes;
- il fait des relevés des maladies et des insectes ravageurs des forêts canadiennes;
- il fournit de l'information, des analyses et des conseils (quant aux politiques) concernant l'économie, l'industrie, les marchés et le commerce reliés au secteur forestier;
- il favorise les occasions d'emploi et de formation universitaire et technique dans le secteur forestier;
- il encourage les Canadiens à prendre conscience de tous les aspects du secteur forestier.

Forêts Canada entretient des rapports sur une base régulière avec les gouvernements provinciaux et territoriaux, l'industrie, le monde du travail, les universités, les environnementalistes et le public par l'entremise d'organismes comme le Conseil canadien des ministres des Forêts, le Conseil consultatif du secteur forestier, le Conseil consultatif de la recherche forestière du Canada, le Comité de l'Inventaire des forêts du Canada, le Comité canadien de la gestion des incendies de forêt, le Centre interservices des feux de forêt du Canada et des comités consultatifs régionaux. Forêts Canada joue également un rôle actif dans des organismes internationaux de foresterie comme l'Union internationale des instituts de recherches forestières et l'Organisation pour l'alimentation et l'agriculture, de même qu'au sein de délégations de nature technique ou commerciale.

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Sponsored by
Environment Canada — Canadian Forestry Service
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Cooperating Agencies
Canadian Pulp and Paper Association
American Paper Institute
National Forest Products Association
Canadian Institute of Forestry
Society of American Foresters
Canadian Forestry Association
American Forestry Association

Editors
P.J. Rennie and G. Robitaille

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CONTENTS

1 Foreword

3 Welcoming Remarks

Dr G. Paillé, Director-General,
Laurentian Forestry Centre

4 Opening Address

The Honorable John Roberts,
Minister of the Environment

9 Welcoming Remarks by Sponsors of Conference

Mr Keith R. Shea, Associate Deputy Chief, Research,
United States Department of Agriculture, Forest Service

11 Mr F.L.C. Reed, Assistant Deputy Minister, Canadian Forestry Service

13 Welcoming Remarks by Cooperating Agencies

Dr T.S. McKnight, Executive Director, Canadian Forestry
Association. On behalf of:
Canadian Institute of Forestry
Canadian Pulp and Paper Association
Canadian Forestry Association

14 Dr J.C. Barber, Executive Vice-President, Society of American
Foresters. On behalf of:
American Forestry Association
National Forest Products Association
American Paper Institute
Society of American Foresters

15 General Overviews

17 The Acid Rain Phenomenon
H.C. Martin

21 Acidic Atmospheric Deposition in Eastern North America:
Forest Resources at Risk
H.H. Krause

29 A Forest Industry Perspective on Acid Deposition
E. Gonick

32 Invited Banquet Address

Forest Decline in Central Europe — Occurrence and Possible Causes
P. Schütt

33 Technical Session I
Pollutant Deposition to Forest Ecosystems

35 Wet Deposition to Forests
P.W. Summers

55 Dry Deposition and Ambient Concentrations
H.H. Neumann, G. den Hartog and N. Bussières

95 Technical Session II
Effects of Acid Rain on Forest Vegetation

97 Effects of Acid Rain on Forest Vegetation: Morphological and Non-mensurational Growth Effects
K.E. Percy

112 Physiological and Biochemical Effects of Acid Deposition on Forest Vegetation
M. Treshow

121 Photosynthesis of Woody Plants: The Impact of Acidic Pollutants, Oxidants, and Heavy Metals
K.F. Jensen

131 Technical Session III
Effects of Acid Rain on Forest Vegetation

133 Recent Changes in the Growth of the Forest Trees in the Northeastern United States
A.H. Johnson, T.G. Siccama and A.J. Friedland

153 Sensitivity of Forest Plant Reproduction to Acid Rain
R.M. Cox

170 Interaction of Forest Canopies with Air Pollutants - Processes and Rates
B. Ulrich

171 Luncheon Address: The Power of Words – Some Examples
M. Lortie

175 Technical Session IV
Effects of Acid Rain on Soil Processes

177 Acid Rain and the Buffer Capacity of Forest Soils
J.W. Hornbeck and C.A. Federer

187 Solubility and Mobility of Aluminum by Acidification of Soils
S. S. Singh

193 The Nature, Forms and Transformations of Sulphur in Soils
J.W.B. Stewart and J.R. Bettany

207 Technical Session V
Effects of Acid Rain on Soil Processes

209 Acid Rain Effects on Nitrogen Availability from Litter and Organic Matter Decomposition
M.K. Mahendrappa

230 Effects of Acidic Precipitation on Foliar and Root Diseases, Soil-borne Pathogens, and Ectomycorrhizae of Forest Trees
R.I. Bruck and S.R. Shafer

232 Evolution of Forest Soils of Quebec under Acid pH Conditions
C.R. De Kimpe

249 Technical Session VI
Implications of Acid Rain for Forest Ecosystems

251 Acid Deposition and Element Cycling in Eastern North American Forests
N.W. Foster, J.A. Nicolson and I.K. Morrison

266 Chemical Characteristics of Precipitation, Stream Flow, Lake Water and Sediments Quality in Northern Temperate Forest Watersheds Threatened by Acidic Atmospheric Inputs
M. Ouellet, H.G. Jones and J.C. Auclair

303 Acid Stress on Forest Habitats: Implications for Terrestrial Wildlife
R. K. Schreiber and K.L. Fischer

321 Technical Session VII
Implications of Acid Rain for Forest Ecosystems

323 Resource Sensitivity Assessment
W.W. McFee

329 Acidic Deposition and Air Pollution: Implications for Forest Management
G.K. Voigt and J.R. Boyle

336 Multiple Use Implications of Acid Rain and Forest Resources
J.R. McClenahen

347 Technical Session IX
Closing Address

349 Closing Remarks
F.L.C. Reed

Technical Session X
Introduction to Field Tour of Catchment Basins

353 The United States Experience in Using Experimental Watersheds in Acid Rain Research
R.S. Pierce

355 Field Tour and Catchment Basin Approach: Canadian Experience
P.J. Rennie

358 Lake Laflamme Catchment Basin: Excursion Guide
G. Robitaille

379 Poster Papers

381 Modelling and Verifying the Effects of Acid Precipitation on Soil Leachates
P.A. Arp and S. Ramnarine

382 Analysis of Percolates From an Acidified (H_2SO_4) Humo-Ferric Podzol
R. Boutin, D. Laflamme and G. Robitaille

383 Effects of Acid Deposition on Soil and Litter Properties: Lysimeter and Field Studies
K.A. Brown and R.A. Skeffington

391 Impacts of Acid Rain on Two Forested Watersheds in Haute Ardenne, Belgium
P. Buldgen and J. Remacle

400 Soil and Bedrock Characteristics of Eastern Canada: Acidic Deposition and Implications for Forest Productivity
D.W. Cowell and A.E. Lucas

409 An Experiment to Assess the Sensitivity of Soil to Acidification
D.E. Dimma, M.A. Griffith and S.N. Linzon

418 Relative Frequency of the Durations and Volumes of Ambient Rainfalls in the Eastern United States
L.S. Evans

419 Ion Transfer Through a Tolerant Hardwood Canopy, Turkey Lakes Watershed, Ontario
N.W. Foster and J.A. Nicolson

428 Heavy Metal Concentration in the Food Chains of Deciduous Forest at Niepolomice, Southern Poland
K. Grodzinska

429 Time Trends in Selected Chemical Characteristics of Streamflow from an Undisturbed Watershed in West Virginia
J.D. Helvey and J.N. Kochenderfer

438 Distribution of Airborne Pollutants Within a Forest System: Effects of Metal and Sulfur Dioxide Deposition on Vegetation and Soils
G. Hogan and D. Wotton

439 Forest Soil Acidification in Southern Finland
S. Huttunen and M. Karhu

440 Composition of Throughfall from Variable Forest Cover Types Exposed to Acid Rain in Central New Brunswick
R.C. Ingersoll and H.H. Krause

441 Chemical Characteristics of Sequential Acid-Rain Episodes, Canopy Throughfall and Streamwater Quality in a Yellow Birch Stand, Laurentides Park, Canada
H.G. Jones, J.C. Auclair, D. Cluis and M. Ouellet

464 Seasonal Precipitation Chemical Characteristics and their Influence on Stream and Lake Waters in the Laurentides Park Region of Quebec, Eastern Canada
H.G. Jones, J.C. Auclair, D. Cluis and M. Ouellet

465 Growth and Nutritional Responses of Yellow Birch Seedlings on Component Mineral Soil Horizons to Acid "Rainwater" Solutions
R. Koppenaal, V. Timmer and D.C.F. Fayle

466 Resistance of the Caribou Lichen (*Cladina stellaris* (Opiz.) Brodo) to Growth Reduction by Simulated Acid Rain
M.J. Lechowicz

474 Influence of Acidification on Metal Uptake by Plants
E. Løbersli and E. Steinnes

485 Direct and Indirect Acid-induced Changes in Foliar Chemical Content
J.L. Malanchuk, J.R. Rhea, E. Engelbride, B. Smyth and W.H. Miner

495 Changes in Acid Flux Through Forest Canopies
H.G. Miller, J.D. Miller, J.M. Cooper and C.A. Flower

501 Significance of Nutrient Cycling Processes in Forest Ecosystems in Altering Acid Rain Effects
M.K. Mahendrappa

507 The Impact of Acid Rain on the Subarctic Woodland Soils of Eastern Canada
T.R. Moore

508 Biomass and Macroelements in a Tolerant Hardwood Stand, Turkey Lakes Watershed, Ontario
I.K. Morrison

517 Effects of Artificial Acid Rain on Percolate Chemistry of Two Jack Pine Forest Soils
I.K. Morrison

526 Ion Movement in Terrestrial Basins in the Turkey Lakes Forest Watershed
J.A. Nicolson

532 The Interaction Between Mobile Anions and Aluminum in a Shallow Podzol
S. I. Nilsson

539 Impacts of Atmospheric Pollutants on Lake Sediments Since 1940
M. Ouellet and H.G. Jones

540 Snow as an Indicator of Atmospheric Fluoride Contamination
M. Ouellet and H.G. Jones

548 Acid Rain, Drought, and Red Spruce Growth Responses
L.J. Puckett

562 Alteration of Precipitation Chemistry by Deciduous and Coniferous Canopies
L.J. Puckett and M.M. Kennedy

569 Incident Rain Characterization
G. Robitaille and D. Laflamme

570 Spatial Variations in the Precipitation Chemistry in a Boreal Forest
G. Robitaille and D. Laflamme

571 Chemical Effects of Simulated Acid Rain on Two Forest Soils
G.K. Rutherford, S.F. Mortensen, J.A. Hern and G.W. vanLoon

578 Cuticular and Dendrochronological Features as Indicators of Environmental Pollution
G.K. Sharma

583 Potential Effects of Acid Precipitation on Forest Wildlife
G.G. Shaw and K.L. Fischer

584 Foliar Buffering Capacity in Boreal Species: Sources of Variability and Potential Use of Buffering Capacity for Indexing Species Sensitivity to Acidic Pollutants
S.S. Sidhu

597 Does Ozone Disturb Water Balance in Forest Trees in Sweden?
L. Skärby and B. Berglind

601 Effects of Ozone on Scots Pine (*Pinus sylvestris*) and Spruce (*Picea abies*)
L. Skärby and B. Berglind

602 Heavy Metal Contamination of Terrestrial Ecosystems from Long-range Atmospheric Transport
W. Solberg and E. Steinnes

612 Microbial Transformations of Sulfate in Forest Soil: Acid Rain Implications
W.T. Swank and J.W. Fitzgerald

613 Microbial Incorporation of Sulfate into Organic Matter in Forest Soils
W.T. Swank, J.W. Fitzgerald and J.T. Ash

621 Stratifying Wet Atmospheric Deposition Samples
E.S. Verry and A.R. Harris

629 Glossary of Terms

Vegetation

Soils

633 List of Participants

FOREWORD

This volume contains papers presented at the "Acid Rain and Forest Resources Conference", held in Ste-Foy, Québec over the period 13 to 17 June 1983. There are over 30 invited papers and 27 papers and 15 abstracts prepared from over 40 volunteer posters.

The Conference was sponsored jointly by the Canadian Forestry Service and the United States Department of Agriculture Forest Service. There were seven cooperating forest industry and professional agencies, identified below. Participants numbered over 250 from eight countries and included over 30 journalists.

Acid rain and long-range pollution have been the focus of several conferences during the past decade, but for North America the last comprehensive and fully open scientific conference in the terrestrial and forestry area was convened in Columbus, Ohio in 1975. In a fast-moving area, therefore, and for one where the threat to forest resources has taken on a high-profile and contentious aspect, it seemed timely to take stock of the present state of scientific understanding. There seemed a particular need to include the relevant Scandinavian and Central European experience and to present the information in an objective and understandable way. Those in government, industry and elsewhere responsible for the well-being of the forest resource, and those dependent upon it for socio-economic values, look to the specialist for informed and clear analyses.

Additional reasons explain the co-sponsorship of the USDA Forest Service and the CFS. In both the United States and Canada forest resources are of major economic importance and have indirect value for wildlife, water quality and recreational activities. The two Services have long-established working relations in areas of common interest and have recently signed a formal Memorandum of Understanding to facilitate collaborative research programs.

The choice of Québec City was explained by several considerations. More of Québec's forests are exposed to higher levels of acid deposition than for any other province. The easily reached Laurentides Park catchment basin well exemplifies the Canadian boreal forest, and the Laurentian Forest Research Centre was able to provide through its acid rain and other expertise much of the necessary organizational support.

The Conference had two main aims:

(i) To review the current state of knowledge on the effects of acid deposition on forest resources, with special reference to the north temperate and boreal forests of eastern North America.

(ii) To broaden the awareness of acid deposition effects, including those of oxidants and heavy metals, in the North American forest community.

Several factors influenced the particular design of the overall program. These included:

(i) making widely available the most authoritative views that could be assembled on the wet and dry deposition levels of the main pollutants, so that valid comparisons could be made among different geographical regions, and appropriate emphasis given to different pollutants in different regions;

(ii) the consideration of forest resources in their widest sense - as sources of fibre and direct economic wealth; as shelter and browse for a diversified wildlife; as stabilizers of water flow and quality; as major mediators between pollutant deposition from the atmosphere and its eventual incorporation into lakes and rivers; and as an expression of unsurpassed aesthetic value underpinning an important tourist industry;

(iii) the compilation of the current state of knowledge and ramifications of the subject area, as revealed by the scientific literature, expressed concerns, and the topics emphasized in previous conferences;

(iv) the general difficulty in the forestry sector of quantifying regional acid deposition effects through the frequent absence of obvious symptoms. This necessitates attention to the more deep-seated ways by which forest ecosystems might be affected - nutrient cycling patterns, basic plant processes, susceptibility to insect and disease attack and soil weathering, which in the long term may profoundly influence site productivity;

(v) the wish, as in all scientific conferences, to have presented the most objective and authoritative reviews of the various sub-topics. These would serve as source material for scientific journalists and other interpretive writers. The aim was to let the science speak for itself, without the passing of resolutions of a political nature. Almost all scientists involved, however, are well aware of the difficult ultimate tasks of quantifying acid-deposition effects, of specifying rates of degradation for different soils and forests, and of suggesting ceiling deposition levels for different pollutants.

Although many people and agencies contributed to the success of this international Conference, special thanks must go to the members of the Conference Steering Committee. Their names and roles were:

Dr G. Paillé, Chairman, Director, Laurentian Forest Research Centre, Canadian Forestry Service, Ste-Foy, Québec
Mr C. Gendreau, Arrangements, Laurentian FRC
Dr G. Robitaille, Posters and Field Tour, Laurentian FRC
Dr P.J. Rennie, Program, Canadian Forestry Service, Ottawa
Dr J. Corliss, USDA Forest Service, Washington, DC
Ms F. Côté, Finance, Laurentian FRC
Ms L. Drouin, Spouses, Laurentian FRC
Dr L.W. Carlson, Canadian Forestry Service, Ottawa
Mr B. Barry, Information, Environment Canada, Québec
Ms B. O'Connor, Information, Environment Canada, Ottawa
Dr R. Doucet, Canadian Institute of Forestry
Mr D.E. Barron, Canadian Pulp and Paper Association
Mr J. Thorner, National Forest Products Association/American Paper Institute
Mr S. Masse, Executive Secretary, Canadian Forestry Service, Ottawa

Special mention must also be made of the seven cooperating agencies and their representatives. They were:

Canadian Pulp and Paper Association - Mr D.E. Barron
American Paper Institute - Mr J. Thorner
National Forest Products Association - Mr J. Thorner
Canadian Institute of Forestry - Dr R. Doucet
Society of American Foresters - Dr J.C. Barber
Canadian Forestry Association - Dr T.S. McKnight
American Forestry Association - Mr R.A. Resler

The production of this volume would not have been possible without the unstinted assistance of the CFS Laurentian Forest Research Centre and the HQ Scientific Editorial Section.

Peter Rennie
Gilles Robitaille

Welcoming Remarks

Dr. G. Paillé, Director-General
Laurentian Forestry Centre

It is my pleasure to welcome you to this International Conference on Acid Rain and Forest Resources. This conference is co-sponsored by Environment Canada through the Canadian Forestry Service and by the USDA Forest Service. We have also obtained the collaboration of important Canadian and American forestry organizations. These organizations are The Canadian Pulp and Paper Association; The Canadian Institute of Forestry; The Canadian Forestry Association; The American Paper Institute; The National Forest Products Association; The Society of American Foresters; and the American Forestry Association.

In organizing this conference we had two main objectives in mind. The first was to review the current state of knowledge on the effects of acid deposition on forest resources, with special reference to the north temperate and boreal forests of eastern North America. The second objective was to broaden the awareness of the effects of acid precipitation, including those of oxidants and heavy metals in the North American forest community.

It is now my pleasure to introduce the Honourable John Roberts, Minister of the Environment, whose portfolio includes both Acid Rain and Forestry. Mr. Roberts has served as Environment Minister for three years. He was first elected to the House of Commons in 1968. He has served as Chairman of the House of Commons Sub-Committee on Peace Keeping and United Nations, Program Secretary to Prime Minister Trudeau, and Minister of State for Science and Technology from 1980 to 1982. In 1982 he was appointed to the Cabinet Committee on Priorities and Planning. He is also Chairman of the Cabinet Committee on Communications. A native of Hamilton, Ontario, Mr. Roberts graduated from the University of Toronto. He studied at the École Nationale d'Administration in Paris and obtained his doctorate from Oxford University. Mr. Roberts makes no secret of the fact that he considers acid rain a very serious problem. He has committed considerable personal time and effort in bringing to light all the developments on this issue. Under his leadership Canada and the United States signed a Memorandum of Intent on Transboundary Air Pollution in August 1980. Finding a solution to air pollution continues to be one of his most important priorities. Mr. Robert's forestry experience goes back to 1966 and 1968 when he served as Executive Assistant to the Honorable Maurice Sauvé, then Minister of Forestry and Rural Development. Now, as Minister responsible for forestry in Canada, his commitment to the development of the forest resource has resulted in several achievements. In 1980 he released the forest sector strategy for Canada which laid the groundwork for new federal initiatives in support of forest renewal, research and development, and forestry student training. We are honored to have Mr. Roberts here today to officially open this 1983 Conference on Acid Rain and Forest Resources.

Opening Address

The Honorable John Roberts, M.P.
Minister of the Environment
Ottawa, Canada

It is a pleasure to welcome to this conference on acid rain and forestry so many distinguished representatives. I wish to extend a particularly warm Canadian welcome to those of you who come from the United States and Europe and who may be visiting this historic city for the first time.

If you know a little about Canada's development you may realize that Quebec is an especially appropriate location for this conference. The word "Quebec" is of Algonquin Indian origin and means "a narrowing of the river". For close to four hundred years, many chapters of Canada's colorful history were played out on the rivers and in the forests of this province in which lumbering formed the mainstay of the economy. And, although the focus of Quebec's forest industries has changed over the centuries, first from exporting squared timber to producing sawn lumber, then from sawn lumber to pulpwood, the resource from which it all came has remained as important to Canada today as it was four hundred years ago.

Together, the six provinces that constitute Canada's forestry sector produce $23 billion worth of shipments annually, with exports amounting to $13 billion per year. That represents 16 percent of this country's total export. No other industry contributes as much to our balance of payments. Forestry also contributes some $3 billion in annual taxes and directly or indirectly employs one million persons, which translates to one in every ten jobs.

In addition, our forests provide the setting for a multi-billion-dollar recreation and tourism industry. And of course we cannot overestimate the environmental value of the forest cover itself: its ability to regulate the flow of many of our river systems, thereby preserving fish habitats; its function in preventing soil erosion; its role as home to a diversified range of wildlife.

As Minister of the Environment, I am responsible for conserving and enhancing Canada's renewable resources and promoting their wise use. To ensure that this responsibility is carried out in a manner consistent with economic and social benefit, the policies that my department follows are formulated within the concept of "sustainable development".

When we apply this concept to forestry practices, we are faced with a problem. For years we have relied on a well-established formula known as "the annual allowable cut" to incorporate the principle of sustainable yield and to calculate the frequency of harvests. Unfortunately, it is now clear that this formula is only as dependable as the data on growth rates, insects, disease and fire loss, regenerative ability, accessibility and so forth that go into making up the formula. However, in 1981, the downward revision of the annual allowable cut levels was so substantial that provinces have either attained or exceeded the limits, or have been unable to attain them because forest reserves were inaccessible for economic reasons. All our provinces now face local shortages of wood.

My department has now embarked on a strategy to strengthen, in cooperation with the provinces and the private sector, the forest resource base.

To begin with, the Canadian Council of Resource and Environment Ministers (CCREM) has endorsed a 40 percent increase in harvest level by the year 2000. This increase, which amounts to 210 million cubic metres, is equivalent to an annual average increase of just 1.8 percent calculated from 1980. This increase closely parallels the average annual increase of 2.1 percent that FAO has estimated will represent the increase in global demand and consumption of industrial roundwood over the same period.

We plan to accomplish this increase by encouraging fundamental changes in traditional attitudes regarding forest exploitation.

Over the past two years since Cabinet approved the *Forest Sector Strategy for Canada*, federal support and funding for the forest sector increased significantly in the areas of human resources, research and development, forest renewal, job creation under Section 38 of the U.I. Act, administration of the forest resource development agreements (formerly with DREE), and forest fire suppression.

The 1982 framework for forest renewal paper that I issued, and which was supported by all provincial forestry ministers under the Council of Resource and Environment Ministers, forecast that combined industry and government spending will have to be $650 million annually within five years. This is based primarily on a program of regular, sizeable increases in replanting of current cutovers and increases in silvicultural treatments. The combined spending program of federal and provincial governments and industry would grow from $240 million in the first year of the five-year program to the target of $650 million.

The federal government is moving into direct support of forest renewal. We have approval in principle to spend a minimum of $130 million a year by 1987 for forest renewal and silviculture practices. This compares with $50 million in 1982.

The forest strategy in 1981 outlined the need for a concern for the improved development of human resources in the forestry field. We have brought forward an increase which was announced in the Spring of 1982 of over $15 million in support of human resources development.

We increased the support going to forestry schools throughout the country from just under $300,000, by adding another $1 million for the year 1982-83–in support of the forestry faculties across the country, at the University of New Brunswick, the University of Laval, the University of Toronto, the University of Lakehead, the University of Edmonton and at the University of British Columbia. We have added $3.5 million in support for forestry schools in contract research and development, and for the employment of 300 summer students in 1983-84. Support in the development of human resources will increase to $6 million in expenditure in 1985-86.

In order to improve our research capability, which was another aspect we focused on in the discussion of the forest sector strategy, we brought forward funding proposals for strengthening our efforts. We have signed research agreements with over half the Provinces to ensure there are neither overlaps nor gaps in our mutual research activities. By the end of this year we expect to have signed research agreements with all ten of the Provinces. We have increased our expenditures on research and development in the Canadian Forestry Service by $5.5 million for the year 1983-84.

One of the major ways in which we have responded to the forest challenge was our commitment in September, 1982 to enter into arrangements with each of the Provinces in support programs to meet the reforestation needs of the Canadian industry. Over the next two or three years we intend to sign a forest renewal agreement with each Province, as we have already with the Province of Nova Scotia. An agreement with Prince Edward Island is ready to be signed. We will assist and encourage the Provinces and the private sector to cooperate in the needed objective of reforestation.

A few moments ago I touched upon job creation. Under the Unemployment Insurance job creation program we have added something like $35 million for 1982-83 alone in the forest sector of capital expenditures to assist with employment in the forest industry. It is short-term employment but it will have consequences for the longer term by improving Canada's wood supply. Obviously that $35 million is in addition to the $170 million which comes from Unemployment Insurance Commission. To date, if memory serves me well, something like 11,000 to 12,000 positions have been created in the forest industry as a result of that program.

We recently announced a very considerable expansion of our funding of capital development of our research institutions all across the country. We made the commitment to go ahead with the Maritime Forest Research Centre in the Maritime forest complex in New Brunswick. We are committed to considerably expanding our research facilities in Ste. Foy, in Sault Ste. Marie, and in Victoria.

Of course, it is not satisfactory to do research and undertake reforestation without taking into account the need to protect the forest resource. That is why the federal government is committed to support the acquisition of supplementary water bomber fleets across the country to provide a much more effective response to forest protection needs in Canada. This is an initiative we took as a response to the requests flowing to us from provincial Governments.

However, we must also emphasize issues that may influence the achievements of our forestry objectives. These include toxic chemicals, acid rain, energy, the land resource base and climatic change.

Among these issues, acid rain probably poses the most immediate external threat to Canada's forests. As you are aware, there is evidence that both wet and dry acid deposition affects forest productivity. Four important international studies since 1978 have unanimously concluded that acid rain could sooner or later irreversibly impoverish many forest sites. Scientists are telling us that large amounts of acid-forming emissions are generated in the North American and European Continents, and that downwind from their sources one can measure high acidity in precipitation and high levels of deposition. They are pointing out that enormous areas of forest in Canada, the United States and Central Europe are being subjected to acid deposition stress that is quite recent. They are warning us that there is increasing evidence that tree growth may be being impaired through the multiple effects of acid rain acting in combination with ozone and sulphur dioxide. A recent study in the Province of New Brunswick has shown that the morphology of seedlings can be damaged at higher pH levels than we previously thought possible.

There's also plenty of bad news about our water resources as well. Our own studies have shown that 4,600 lakes are dead – meaning that their acidity level is too high to support fish life. Another 12,000 are moving toward the same condition. At the rate we are going, we'll soon be in the same position as Sweden, with its 20,000 dead lakes, or the American States east of the Mississippi, where, according to the Congressional Office of Technological Assessment, 18 percent of the lakes and 21 percent of the stream miles in the area show acid rain damage. Some of the best-documented acid rain losses to sportfishing stocks are American losses. These include elimination of all fish in 180 lakes in the Adirondack vacation area of upstate New York.

The time has come to stop wringing our hands as we record the relentless totals coming in: we must act to reduce acid deposition and pollution levels now, before the damage becomes irreversible. In fact, it is hard to understand what we are waiting for. Hasn't recent environmental history taught us anything? Can we really have forgotten already the lessons of Silent Spring, the bumper stickers saying "Lake Erie died for your sins" and the whole environmental awakening of the 1960s? Experience taught us then that the price of environmental neglect may be deferred, but it must be paid eventually – and, like our credit card bills, the longer we wait, the higher the price gets.

So what are we waiting for? Some people say we need more data, that we don't know enough to act wisely, that we cannot apply what we have learned so far about damage to our ecosystems to others we have not studied. What we need, they say, is more research.

I am certainly in favor of more research. However, I also know that we learned an invaluable lesson in the early 1970s. Those were the years in which we knew that eutrophication was choking Lakes Erie and Ontario, but were unable to precisely pinpoint the cause: was it nitrogen or phosphorus? Some scientists felt we required a 75 percent reduction in phosphorus concentration, others felt 40 percent would do it, still others felt more research was necessary. Finally, a political decision was made to begin reducing phosphorus discharges at the sources. In the end, the actions will require some revision, but meanwhile, a commendable and effective start was made on the rehabilitation process.

That process involved dealing with an escalating environmental problem on the basis of managing risk, of taking decisions with necessarily limited scientific understanding – limited in the sense that at the time the decision must be made, scientific knowledge was not yet complete and would undoubtedly produce further useful data later.

In my opinion, we are now in the same position with regard to acid rain. We are ready to deal with acid rain on the basis of managing risk, using the knowledge we have so far.

Let's look at the situation more closely. We know there is widespread acceptance of a threshold deposition figure that separates damaged water bodies from undamaged. Many scientists are confident that this figure could serve as the basis for an abatement strategy that would lead to the rehabilitation of damaged lakes. If we can achieve 20 kg/ha/year, that should go a considerable way towards protecting moderately sensitive lakes and streams.

Making a start on protecting our forests won't be quite as simple. Scientists do not yet feel they can suggest a tentative threshold deposition level. If, as many believe, our lakes and streams are the most sensitive part of our environment to acidification, the 20 kilogram target may protect our forests. If we find our forests and soils are more sensitive than aquatic ecosystems we will have to revise our objective.

We do, however, have general guidelines for the development of an initial course of action. Within the last two months, the Canada/US Working Group set up to study acid rain under a Memorandum of Intent between these two countries published a report that contained six basic findings:

1. Damage is being done to aquatic systems in both countries;
2. This damage is being caused by sulphur emissions;
3. The depositions and damage are downwind of major industrial sources of SO_2;
4. In areas receiving depositions of 20 kilograms per hectare per year or more, you find damage. Below that level, you don't;
5. The answer to the problem is to control SO_2 emissions;
6. If we don't control such emissions, they will increase to the end of the century.

On the basis of this report and other evidence, we have made a specific proposal to the United States. This proposal rests on two main premises:

First, we need to reduce sulphate deposition to less than 20 kilograms per hectare per year.

Second, computer modeling has shown that to get sulphate deposits down to 20 kilograms per hectare annually, we need to reduce emissions by 50 percent.

We are seeking agreement from the United States on two main points: that the premises I have just outlined are valid; and that we join hands in a program to bring emissions down by 50 percent.

This approach respects both economic and environmental imperatives. The target date over approximately the next decade gives industry time to adapt or benefit from cheaper abatement systems that may be developed by then. Equally important, this is a plan that focuses on results, rather than methods.

The cost to Canada would be $1 billion annually. For Americans, the costs would be about $2.5 to $4.5 billion annually. It is certainly encouraging to note that repeated polls have shown Canadians give overwhelming support to cleaning up acid rain.

Will we be able to get a joint program under way in time? While I can't claim things are moving quickly, there are some hopeful signs. One is the growing sense that the American public is awakening to the acid rain danger. Another is the forthcoming approach I observed in the new American Environmental Protection Agency Administrator, William Ruckelshaus, during my recent meeting with him in Washington.

Meanwhile, it's up to the forest scientists to meet the challenge of finding the information we politicians must have if we are to continue the fight. You are the authorities who can tell us what needs to be done to protect the forests. You can put dimensions on the problem. You can give us the figures for ceiling deposition levels for different pollutants.

The increasingly challenging problems of today call for the pooling of scarce expertise and the stimulus of international contact. Conferences such as this one are ideal for this purpose. The knowledge shared here, the springboard for more explorations that your discussions will provide, will lead to further information on which policy makers can base their decisions.

I know that you are as committed as I am to solving these problems. Several weeks ago I heard George Tomlinson from Domtar Inc. give an address to the American Association for the Advancement of Science in Detroit. He presented some alarming evidence on the effects of acid rain on the forests in West Germany. I know that some of the German scientists Dr. Tomlinson quoted in his address are here at this conference and it will be interesting for you to learn from their experience. I am positive that, like me, you don't want the forests and waters of all our respective countries to end up in the same condition as those of West Germany, where recently released reports claim up to 50 percent of the forests are in danger.

And I am confident that any profession that can gather together so distinguished an international audience for such an interesting and comprehensive program will certainly be able to produce the hard data we require. We all eagerly await the results of your efforts.

Welcoming Remarks by Sponsors of Conference

Mr. Keith R. Shea
Associate Deputy Chief, Research
USDA Forest Service

I bring best wishes from Chief Max Peterson, and his regrets that he cannot be here in person. I know that he shares your concerns about acid rain and other atmospheric pollutants affecting natural resources. He anxiously awaits the results of this conference.

Over the last 200 years, Canada and the United States have shared many things - a common border, a common heritage, and a united devotion to democracy and the welfare of our two peoples. Today, we also share concerns about acid rain, which has become a major issue in both our countries and throughout many parts of the world. In the southeastern Canadian provinces and in the eastern United States, we have been faced with the problem of acid precipitation for some time. We need to determine whether there are serious terrestrial effects, their causes, and remedial measures.

With the far-reaching implications of the acid precipitation issue, you face quite a challenge at this conference. From the looks of the program, you are well able to meet that challenge. Seldom have I seen such a remarkable team of scientific minds assembled to discuss an issue that draws such worldwide attention as does acid rain. The format of this conference is broad enough to allow many scientific considerations, since it includes formal papers, poster sessions, and panel discussions.

You are fulfilling one of the most vital roles of the scientific community in a complex, modern society. You are presenting the facts which decision makers and the public desperately need. We need good data on which to base good decisions. We need good data that the media can use to inform our publics. Acid rain is a scientific fact. Your purpose here is to explore that aspect of acid rain. But acid rain is also a public issue. Your findings can illuminate that issue and provide a factual basis for making rational decisions. Those decisions will be difficult ones. They must be based on all aspects of the acid rain issue: the scientific and environmental, the economic, and the political.

We need to have, first of all, a definition of the problems, and their extent. Where problems are identified, we need information on alternatives for solving them. The bottom line, for the people of Canada and the U.S., is: How can we enjoy the fruits of progress, and still alleviate adverse effects of acid rain and other man-caused pollutants? This conference promises to go a long way toward giving us that answer.

We already have valuable data from several other conferences. For instance, some of you participated in the 1975 International Symposium sponsored by Ohio State University and the Forest Service to assess what was known about acidity in precipitation and to focus attention on its ecological effects throughout the world. It was a forum for academic, industrial, governmental, and public interest groups to meet and debate the magnitude, extent, nature, and consequences of acid precipitation.

Today, this scientific conference builds on the results of the Ohio State conference and others, to focus on:

1. Reviewing the current state of knowledge on the effects of acid deposition on forest resources, with special reference to the north temperate and boreal forests of eastern North America.

2. Broadening the awareness of acid precipitation effects, including those of oxidants and heavy metals, in the North American forestry community.

As joint sponsors of the conference, the Canadian Forestry Service and the USDA Forest Service are again carrying on the tradition of cooperation among two friendly neighbors, concerned about the future of our natural resources and the well-being of both our peoples.

I also want to acknowledge the special efforts of Dr. Gilbert Paillé, Director of the Laurentian Forest Research Centre of the Canadian Forestry Service, and of Dr. Peter Rennie, Chairman of the Conference Program Committee. I should also like to thank Dr. John C. Barber, Executive Vice-President of the Society of American Foresters, and Mr. K.A. Armson, Chief Forester of the Ontario Ministry of National Resources, who are representing the cooperating groups which have helped make this conference possible.

I want to acknowledge the presence of scientists and authorities from western Europe, to thank them in advance for contributing their knowledge and experience to us in North America. Their experiences are particularly valuable, since some aspects of their environment resemble ours.

I sincerely hope that this joint venture will be as successful as other Canadian-United States projects, particularly those in the Spruce Budworm (CANUSA) program, fire management, and forest product development.

As you seek answers to a question that concerns the people of both Canada and the United States, let me leave you with a thought that was expressed very eloquently by William Kingdon Clifford:

> Remember, then, that science is the guide of action; that the truth which it arrives at is not that which we can ideally contemplate without error, but that which we may act upon without fear; and you cannot fail to see that scientific thought is not an accompaniment or condition of human progress, but human progress itself.

If your science can guide the actions of our two nations in dealing with acid rain, then that truly will be human progress.

Mr. F.L.C. Reed
Assistant Deputy Minister
Canadian Forestry Service

Mr Minister and Mr Chairman, Distinguished Guests, Ladies and Gentlemen: It is my privilege now to welcome you on behalf of the Canadian Forestry Service and at the same time recognize the outstanding effort made by the U.S. Forest Service, the U.S. industry, Canadian industry and professional foresters as co-sponsors of this Conference. I believe this is the first time in the history of acid rain and forestry conferences, and there have been many of them, that we have had this broad base of interest and support.

Now, I welcome you in this context. Forest renewal in Canada is more than just a theme, a policy and it is more than just a slogan. Since 1978, the urgency of renewing Canada's forests has become a matter of high priority, not only with the federal government but with every single provincial government in Canada and with the industry. Canada's forest lands, our forestry resource base, is now recognized as our No. 1 National Asset. Production targets have been set by consensus between industry and the senior governments and, as you heard just a few moments ago, we are striving to increase forest productivity and output in the next twenty-five years by a very substantial figure. I do not believe we have another industrial sector in this country which even begins to offer the promise of forests which are well managed.

It follows from what I have just said that the protection of this forest heritage is absolutely essential. Indeed, I maintain that you might just as well plant trees upside down as to plant them, then not protect them. Now protection in this context embraces fire, insects and disease and acid rain. In the case of fire some of you may not know that we are pretty good at fire in this country. In 1980 and 1981 we burned five, six, seven times as much forest land as we harvested. Perhaps 20% of that was industrial forest land with timber which we hoped to harvest in the normal routine of management planning. That fire situation has to change and we have recently undertaken to inspire the creation of a fleet of water bombers in an inter-agency fire centre and other things which will cope with our fire losses. In the case of insects and disease, we lose annually about two-thirds as much mature timber as we harvest. We know and we can measure the losses from neglect of planting following harvest, and we can measure the impact of fire losses and the impact from insects and disease.

Now we are focusing very heavily on the potential damage from acid rain. The Canadian Forestry Service probably has the most comprehensive, systematic orderly research program of any country in the world when it comes to acid rain and forestry. To date we cannot say with any confidence that we know what the extent of that threat is. In fact, the threat of acid rain to forestry is, in the minds of quite a few people, really quite a contentious issue. For example, in some areas it is suspected that the positive fertilizer effects may indeed outweigh the negative impact. In spite of this, I want to emphasize that we are concerned when we face timber deficits emerging in various areas in this country. Even a minor loss from acid rain is bad news and it would be most unwelcome if we suffered even further losses in addition to those from neglect of planting from fire, insects and disease. So we are concerned and we are spending millions of dollars each year to learn more.

Canada in this case is fortunate to have the full cooperation of the U.S. Forest Service. We have about six bilateral cooperative programs going now, formal project agreements signed at the Ministerial and at the Service level for the exchange of information from Working Groups to the exchange of research findings from cooperative research. These run all the way from forest products right through to insects and disease, spruce budworm, mountain pine beetle and so on. Through cooperation of this nature we find that we can stretch our scarce research dollars much further, get answers more quickly and use our scientific expertise more efficiently.

We are not concentrating, as you can tell from the delegates in this room, solely on cooperation with people in North America; we are also following closely the experience in northern and in western Europe.

With those few remarks Mr Chairman, and with my eye on the clock, I welcome all of you to the Conference. It promises to be a milestone in our search for truth and I would like to go on record as personally facing this challenge with optimism. It was Martin Luther who said

> "If I knew the Apocalypse, the cataclysm were coming tomorrow, I would still go out and plant my apple tree".

So regardless of what you people come up with this week by way of scientific results, I am still going to be out there planting trees across the country and we will protect them with whatever resources we have to muster to do so. Thank you very much.

Welcoming Remarks by Cooperating Agencies

Dr. T.S. McKnight
Executive Director
Canadian Forestry Association

It is an honor and a pleasure to extend a welcome to you on behalf of the three Canadian agencies which have cooperated with the Canadian Forestry Service, Environment Canada, in the preparation of this important meeting.

The first agency is The Canadian Institute of Forestry, whose membership comprises foresters, those in allied sciences and others working in forestry concerned with all aspects of forestry. The Institute Program is primarily directed toward the professional and scientific side. The second is The Canadian Pulp and Paper Association, which is a national association with sixty-five member and associate-member companies in all parts of Canada. It accounts for about 98% of the pulp and paper and paper board produced in Canada. The third is The Canadian Forestry Association, which is a federation of nine provincial forestry associations and which is dedicated to encouraging approved forest utilization and management, of informing the public on the importance of our forest resources and the need for their protection, wise use and management.

These three organizations represent collectively the professional and technical group of foresters and related professional technical persons, also the industry which in terms of export earnings is the most important one in Canada, and finally through the Canadian Forestry Association the general public interested in forests.

Acid rain over the past few years has become virtually a household word. As with other complex topics which are important, there are inevitably some misunderstandings. There is much that we do not know about the effects of acid rain on forests, but there is also much that we do know, from which conclusions may be drawn.

This meeting will serve a most valuable purpose by providing a forum for scientific discussion and by providing perspectives. It will enable you as scientists to inform not only those who professionally or industrially have a clear vested interest in the well-being of our forests, but also the members of the public who directly or indirectly may be affected by the consequences of acid rain.

I think it is particularly important to you in your deliberations to be especially disciplined in the differentiation between facts, what is known about the processes of acid rain and the probable implications of these facts and processes on forest systems. The public and those with very direct interests in our forests must be informed carefully and accurately about acid rain and I am sure that in this meeting you will do much to further this by your presentations and deliberations. Once again a very hearty welcome. Thank you.

Dr. J.C. Barber
Executive Vice-President
Society of American Foresters

Thank you and good morning Ladies and Gentlemen. It is really a great pleasure for me to have been selected to represent these coordinating organizations: The American Forestry Association, which represents the public; The National Forest Products Association and The American Paper Institute, which represent forest industry in the United States; and, of course, my own Society of American Foresters, which represents professional forestry.

We are delighted to be cooperators in what we think is a very significant international event. Each of these organizations is vitally concerned about the environment and each is vitally concerned about maintaining forest productivity. We welcome each of you to this Conference.

That acid rain does fall I think is indisputable, but there is certainly no unanimity about the effects of acid rain upon forest ecosystems. As all of the scientists in the room know, there are tremendous difficulties associated with measuring the effects and the complexities of the forest ecosystem about something such as acid deposition. When you start to look at the confounding and complicating effects of soils and add to that the climatic variations, we find that we are in a really difficult situation in attempting to measure small differences that might take place in forest ecosystems.

Yet I think it is very important that we focus on being able to accurately measure and determine the effects, because simply a reduction in productivity of only a few per cent when it is spread over the millions of acres of forests that may be exposed to acid deposition will have a tremendous economic impact. I think Minister Roberts has already stressed that point. Moreover, we know very little about the cumulative effects over long periods of time, simply because we do not have records and we cannot very well reach back into the past and determine what has happened.

Many of the reservations, of course, about the effects of acid rain are valid differences in judgement. They relate to some rather significant differences of opinion that have been expressed in the scientific community. I think all of us here recognize the importance of quickly building our knowledge of acid deposition, both rain and particulates. We all desire to work toward a better understanding of the problem and to seek solutions.

Now as the Minister previously mentioned, Secretary of State Shultz from the United States and External Affairs Minister MacEachen met in April and they agreed on some procedural matters which will help better utilize the Joint Committee Reports that had been generated previously. They have already agreed to meet again this fall to further discuss the acid rain problem. Certainly I hope that the Ministers can resolve the political aspects of the problem between the U.S. and Canada so that we can all begin to deal with it as a scientific issue of mutual concern.

I think the recent increases in research effort on the parts of both governments are a movement in this general direction. At this time, there are many conferences and briefings going on on acid deposition, both in our countries and in Europe, which testifies to the urgency of finding some answers to the problems that we have before us. You are I think an undoubtedly unparalleled assembly of scientists, who are all authorities in many interrelated fields associated with forest, and forest ecosystems. When we leave here on Friday I think we will probably be the best informed group in the world on acid rain, so on behalf of our co-sponsoring organizations I want to extend thanks and appreciation to the Canadian Forestry Service and, to the U.S. Forest Service who are sponsoring this Conference and to our counterpart associations and institutes in Canada who joined us in our cooperative effort. Thank you.

GENERAL OVERVIEWS

The Acid Rain Phenomenon

Dr H.C. Martin
Senior Advisor
Federal LRTAP Liaison Office
Atmospheric Environment Service

Good morning Ladies and Gentlemen. Some time ago when Peter Rennie undertook the Herculean task of developing a program for this meeting he called me and asked if I could give an Overview Paper on Acid Rain. He had two instructions. He said talk about the acid rain phenomenon but don't discuss forestry. Well, having left the workbench of the scientist some years ago I have developed two characteristics which Peter Rennie so rightly diagnosed. First, I have no intimate knowledge of the state of science in my preferred discipline, and secondly, I have been involved with management and hence have developed the tendency to talk around the subject rather than about it. So I will talk in a general way about the elements of this problem as they exist beyond the forest edge. But I would like to take the opportunity occasionally to make reference to the linkages that exist between the phenomenon and the environments outside the forest and the forest itself, occasionally speaking on the matters that will be discussed more fully in the next few days. I will follow the pollutants from their sources, through the atmosphere, looking at the deposition processes and then briefly looking at the responses in the receiving environments.

First of all, the acid rain issue is a global one. Although we have a near balance between natural emissions of sulphur dioxide and man-made emissions, the distribution is non-uniform. In the northern hemisphere the problem with acidification, using annual pH values as an indicator of acidification, is co-located with the most highly industrialized regions, so that we have our lowest pHs on the eastern part of the North American continent, over central Europe and over Japan – in other words, over the most highly industrialized regions. In the North American Prairies and in central Asia the problem does not arise and the average pH of rain is rather high.

Let us then look at the sources of the problem. How did this situation come about might be the question we should first ask? Some decades ago, three or four, we had a situation where high concentration sources were emitting near the surface of the earth and causing difficulty at ground level. Because of health problems this matter was addressed and in North America we instituted Clean Air Acts in both Canada and the United States. These legislations were designed around ambient air quality standards and resulted in the cleanup of the cities. But as time went on the cities grew from towns into conurbations where there are tens of thousands of emission sources being simultaneously integrated by the atmosphere and being identified downwind for hundreds of kilometres. In addition, there are situations where there are very large point-sources.

In order to meet the requirements within the legislation tall stacks were constructed and material was transported far downwind, such as is the case with a 1,283-foot-high point-source in Ontario. Once emissions have left the stack they are in the realm of the atmosphere where transport, transformation and deposition take place. Three processes involving three disciplines are involved. One is – meteorology - this is the discipline described by less diplomatic critics as "mythology". Then there are the air chemistry transformation processes in the atmosphere, and finally deposition. In eastern North America the general flow is from west to east with some slight difference between summer and winter. The chemistry is a very complex area. The atmosphere is not that well understood in terms of chemical processes. In simplistic terms, sulphur dioxide emitted into the atmosphere is deposited unoxidized in a dry form or it is oxidized. It may react with water before oxidation or after to be deposited in the form of sulphate.

Nitrogen oxides are similarly oxidized. In reality the processes are much more complex because of photochemical effects; a number of other atmospheric parameters also determine the fate of NO_x emissions. The dry component of deposition is roughly as important as the wet component.

To measure surface deposition a network system is required. Because of the concern we have had and the difficulty associated with measuring dry deposition there are not at this time long-standing operational networks recording dry deposition. For wet precipitation there is in Canada at least what is called the Great Canadian Network. It is a composite of many stations in a variety of networks collecting rain samples on a weekly or monthly basis for the analysis of a wide variety of constituents. This national network is linked with the U.S. national network and with co-located stations in Canada and the United States. In this way it is possible to inter-compare data and to make certain that anomalies do not exist in our chemistry. From these networks and the linkages between the U.S. and Canadian networks it is possible to put together maps of precipitation pH or of sulphate deposition. Areas of high acidity or high sulphate deposition are correlated with areas where there are large emissions or where the latter are upwind. This is as might be expected.

Moreover, it is necessary to look at precipitation pH in relation to the receiving environment. Here the question of sensitivity arises. How does one characterize sensitivity? By using soil? By using water? Or by using some other kind of criteria? In spite of this difficulty, it is found that a very large proportion of the sensitive region of eastern North America is exposed to the greatest deposition. The regions that are at risk include upper New England and the eastern central portions of Ontario, Quebec, and the Maritimes. All these regions have shallow soils and little buffering capacity. Rain entering such systems goes into the catchment, then the streams and lakes, with very little alteration to its original chemistry. In the atmospheric component of our studies attempts have been made to sort out, by modelling, emission/deposition patterns. How do such models work? What is taken, for the calculation are all the pollutant-emission sources for the Continent. Included are the meteorological characteristics on a 12-hourly basis for a whole year, the best available chemistry, and the best estimates of the mechanisms for deposition. From a mathematical synthesis of these data a theoretical deposition map is obtained, based on the particular year to which emissions relate. This gives us an indication of what might be expected to happen in the real environment. The models are predictive tools and at this time they are used only for broad geographical regions and for sulphur compounds.

When modellers build their models it is essential to have a linkage with forest scientists so that aspects like the physical structure of a forest and its ability to absorb pollutants are taken into account. Such aspects determine the rate at which pollutants can be removed from the atmosphere. If the linkage is absent the models will not be effective or realistic. The most difficult problem in the atmospheric area are related to the problems of dry deposition, especially the inability to measure it satisfactorily. Moreover the chemistry of the atmosphere is thought by some to behave linearly, but by others non-linearly. If this critical aspect cannot be sorted out a prediction cannot be made on what will happen if emissions are cut by half. Will the deposition be halved or reduced by some other factor? This is a question of key significance to abatement. In Stockholm last year it was agreed that if emissions and deposition are considered on a regional basis then a proportional relationship might be expected.

Once acidifying substances have been deposited effects must be considered. We won't for the moment look at what happens to the rain or the dry deposition that enters that terrestrial black box that Peter Rennie defined for me but will go straight to the aquatic systems and see what happens there. There has been an extremely large focus of attention on the aquatic response to acidification in Canada, the United States and Europe. In Canada the reason for this attention is well founded: there are in eastern Canada 1.7 million lakes. They are largely on sensitive terrain and deposition levels are among the highest received in all of Canada. Another reason for concern about aquatic systems is their much more rapid response to stress than terrestrial systems supporting forests. A loss of fish species can be seen in a single year. Less obvious are losses affecting key elements in the food chain, the invertebrates, and some indicator species that can be detected from making surveys. If the pH in a lake is below 5 no fish can be expected there. Bearing in mind that some of those lakes reflect the rain chemistry nearly directly and that the rain chemistry might be as low as pH 4.2, the prospects for fish populations are not good. Another area of alteration in the aquatic environment is vegetation.

Acidified lakes are invaded by sphagnum moss, a species characteristic of acidic peatlands. In addition, a green coloration is due to filamentous algae. This is seen in some Ontario lakes. This resembles a slime. Overall, the general response in the aquatic environment is one of reduced diversity and population of biological organisms.

So far we have been using sulphur as the main pollutant of concern. Nitrogen, on the other hand, does not appear to make its way into the water but is contained within the catchment surround. Only during spring runoff or heavy rain is nitrogen seen as a component of an acidifying lake. From measurements of sulphur, so-called "targets" have been developed. In North America the target of 20 kilograms wet sulphate per hectare per year seems to be one that is protective of moderately sensitive aquatic systems. In Europe at Stockholm last year a more stringent target was developed which was protective for essentially all systems. Such targets will be subject to considerable refinement and expansion over the next while. Their significance lies in the fact that they provide a number that can be used to assess an aquatic resource at risk. Across eastern Canada there is a set of about 14 stations where intensive measurements of aquatic chemistry are being made. If information from those stations is taken, going from the west to the east, it is found that the target of 20 kilograms is exceeded at all points between Algoma and Halifax. This large area is receiving more pollution than is advisable if the system is not to become acidified.

The acidification problem goes beyond our natural ecosystems into the man-made environment as well. Just down the road from here at the Ministry of Justice in Quebec City can be seen what happens to limestone and sandstone when they are subjected to sulphur dioxide or sulphates in an urban environment. These materials are disintegrating and decomposing. The main materials that we find deteriorating are the masonries and the metals, the galvanized metals and the painted metals. This is not a long-range transportation problem. It is one where effects occur near to sources. But the important point is that the agent, the corrosive agent, is the same as that which is being examined in the natural environment - sulphur. These damages can be quantified and for this reason they are extremely useful in trying to assess in economic terms the implications of the emissions.

There is another area of concern relating to effects and that centres on health. This is an area of considerable controversy. There are perhaps two places where potential indirect health problems have been identified. One is the bio-accumulation of mercury in aquatic systems and eventually in fish stocks. No cases have been found where concentrations of mercury in fish obtained from acidifying lakes were greater than those allowable by health standards, but there are elevated concentrations nonetheless. The other area of concern relating to health effects has to do with the utilization of lake water in cottage plumbing. Where acidic water remains unused for a week or so in copper/lead plumbing systems, it accumulates high concentrations of copper and lead. In such instances, it must be flushed away before a fresh supply can be used for human consumption.

Finally, a comment about agriculture. There has been a wide range of studies undertaken in agriculture to look at the effects of gaseous sulphur dioxide, acid rain itself and oxidants. It is perhaps in the last category that the information is most striking. In southwestern Ontario white beans can become seriously chlorotic within five days of experiencing an episode of phytotoxic ozone concentration. It is not certain what this kind of an alteration in the colouring of the crop does to the quality of the eventual harvest. This is under examination. With regard to effects in the soils themselves the impact of acid rain or SO_2 may be minimal because farmers regularly add amendments and fertilizers to maintain favourable fertility levels.

Mr. Chairman, I believe that covers most of the main components of the acid rain phenomenon. Peter said I should give a "motherhood" paper and I guess this is it. I conclude with only one observation. Mother Nature is not amused. Thank you.

DISCUSSION

Question: In developing target loadings are sulphur species other than sulphate excluded?

Answer: In developing target loadings for sulphate, "sulphate" is taken as a surrogate for all sulphur species.

Question: What target level for sulphur did the 1982 Stockholm Conference suggest for complete protection?

Answer: A target level was suggested in terms "of total sulphur", but if this is converted to "sulphate" for ease of comparison it was 15 kg total sulphate per hectare per year. The one determined for North America was 20 kg wet sulphate per hectare per year. As "total sulphate" comprises some 50-60% wet plus 40-50% dry deposition, it can be seen that the Stockholm target is about twice as stringent.

Question: Are you aware of any papers linking aluminum with health effects?

Answer: No.

Question: Are models able to predict deposition rates from emission data?

Answer: Yes, and the models can be used to predict changes in deposition rates when a group of emission sources are excluded. This is a useful exercise assisting to indicate how best deposition might be reduced.

Acidic Atmospheric Deposition In Eastern North America: Forest Resources At Risk

H.H. Krause
Department of Forest Resources
University of New Brunswick

ABSTRACT

Acidic deposition above natural levels occurs over most of the North American continent east of the 100°W meridian.

With an annual growth of approximately 475 million m^3 of wood in the United States and 146 million m^3 in Canada, the forests of affected areas contribute significantly to the economies of both countries, but especially in Canada where one in ten jobs depends on forestry.

In the United States, about 10% of the annual forest growth occurs in areas now subjected to very heavy acidic deposition and more than 75% is in areas of heavy and moderately heavy deposition. Among the forest ecosystems within the zone of very heavy deposition are sensitive combinations of conifer cover and low-buffering- capacity soils.

In Canada, about 53% of the annual growth is within the zone of light deposition, 43% in zones with moderately heavy and heavy deposition and only 4% in areas with very heavy deposition. But, unlike in the United States, most of the growth is in coniferous or mixed-wood forests, and on soils with low buffering capacity and a susceptibility to aluminum toxicity.

Besides possible effects on the fibre-producing ability of forests, acidic deposition may indirectly affect terrestrial wildlife and aquatic habitats. Whereas information is still inconclusive with respect to forest productivity and terrestrial wildlife, adverse effects of acidic deposition, at present levels, have been proved for aquatic habitats, and a danger now exists for areas with soils and bedrock of low buffering capacity.

INTRODUCTION

Eastern North America, with forests ranging from the southern pine region to the Boreal coniferous belt, has a timber reserve of several billion m^3 and an annual growth in excess of half a billion m^3. The estimated value of the annual growth is $8.3 billion in the United States. This amounts to 70% of the total value of that country's annual forest growth. In eastern Canada, the annual forest growth is estimated to be worth $3.9 billion. Furthermore, the eastern provinces account for about 64% of the value added in the entire forest industry of the country. In addition to their industrial significance, the forests of eastern North America offer habitats to a diverse terrestrial wildlife and contain numerous water bodies, providing a strong recreational potential, the value of which is difficult to measure.

Over the last few decades, forests in major portions of eastern North America have been subjected to increasing levels of acidic deposition. Declining forest growth has been linked indirectly to rates of acidic deposition in at least one instance (Johnson et al. 1981), but the literature so far does not contain conclusive evidence that yield reductions have occurred as a direct result of acidic deposition. However, concern exists because (1) trees are plants with a long life span and offer the possibility for a cumulative impact of pollutants, (2) forests more often than not occur on soils in which nutrients are limited and which are normally not treated with fertilizers or lime, and (3) forest canopies present large surface areas for interception of gaseous and particulate forms of acidic pollutants.

Levels and Distribution of Acidic Deposition

The area affected by above-natural acidic deposition stretches from the southeastern United States to Canada north of the Great Lakes and across Newfoundland. Emission of acid-forming pollutants is concentrated in the eastern Mid-west United States and Ontario, but, due to long-range transport of pollutants by air masses of predominantly northeasterly flow (Altshuller and McBean 1981), acidic deposition also occurs in the far eastern portions of Canada. The areas with very heavy deposition, i.e., where the annual hydrogen ion input ($D_H{}^+$) is greater than 80 mmol m^{-2} and the annual input of sulfate ions ($D_{SO_4}{}^{2-}$) is greater than 40 mmol m^{-2}, roughly coincide with the areas of largest emissions (Bangay and Riordan 1982). Areas with heavy deposition ($D_H{}^+ > 60 < 80$, $D_{SO_4}{}^{-2} > 30 < 40$ mmol m^{-2}) stretch from Tennessee to southern Ontario and also include portions of southwestern Quebec. Moderately heavy deposition ($D_H > 40 < 60$, $D_{SO_4}{}^{-2} > 20 < 30$ mmol m^{-2}) has been recorded as far south as Mississippi, Alabama and Georgia, and to the north in Ontario, Quebec, the southern part of New Brunswick and in Nova Scotia. Finally, acidic deposition at low rates ($D_H{}^+ < 40$, $D_{SO_4}{}^{2-} < 20$ mmol m^{-2}) occurs through most of the remaining part of the United States east of the 100°W meridian and far into northern Ontario, Quebec, southern Labrador and in Newfoundland.

Forest Resources Exposed to Acid Deposition

The area affected by acidic deposition in the United States includes the intensively managed forests of southern pines, the central deciduous forest region, the high-elevation forest of the Appalachian mountain ranges, and the northern hardwood forests of New England and the Lake States. The total forest land in the affected area comprises 145 million ha. Approximately 10% of the combined annual growth of hardwoods and softwoods in the affected area occurs within the zone of very heavy acidic deposition. Over 75% of the growth is within the zones of heavy and moderately heavy deposition (Bangay and Riordon 1982).

In Canada, more than one-half of the productive forest land lies in the eastern part of the country with above-natural acidic deposition. Most of the Boreal Forest Region is exposed to light deposition. Most of the Great Lakes-St. Lawrence, the Acadian and the Deciduous Forest Regions are exposed to moderately heavy and heavy acidic deposition.

According to the Canada forest resources inventory data of 1981 (Bonnor 1982), forestry is the principal if not exclusive form of land use throughout the Boreal Forest Region and the New Brunswick part of the Acadian Forest Region. Agriculture predominates in southern Ontario and parts of southern Quebec, but the major part of the Great Lakes-St. Lawrence region has remained under forest cover.

The Canada forest resources inventory distinguishes between three types of forest: Softwoods, mixedwoods and hardwoods.

- Softwood forests, consisting of pure coniferous stands or stands with an admixture of hardwood of less than 25% by volume, are predominant through most of the Boreal region. Typical cover types are pure jack pine (*Pinus banksiana* Lamb.) or black spruce (*Picea mariana* (Mill.) B.S.P.) or a mixture of both. Stands of these types have originated after fires and more often than not have an admixture of aspen (*Populus tremuloides* Michx.) and paper birch (*Betula papyrifera* Marsh.). Towards the east, balsam fir (*Abies balsamea* (L.) Mill.) gains prominence, forming pure or mixed stands with black spruce or white spruce (*Picea glauca* (Moench) Voss). Another characteristic species is tamarack (*Larix laricina* (Du Roi) Koch), occurring in greater proportions with black spruce, where drainage is poor.

The zone of mixedwood forests, with a hardwood component of 25 to 75%, covers most of the Acadian Forest Region and the southern and northern portions of the Boreal and Great Lakes-St. Lawrence Forest Regions, respectively. In the northern portions of this zone, birch, aspen and red maple (*Acer rubrum* L.) are the principal hardwood species. Towards the south, tolerant hardwoods, including yellow birch (*Betula alleghaniensis* Britton), sugar maple (*Acer saccharum* Marsh.) and American beech (*Fagus grandifolia* Ehrh.) gain prominence. Among the softwood species that occur in mixture with hardwoods are white pine (*Pinus strobus* L.), red pine (*Pinus resinosa* Ait.), white spruce, eastern hemlock (*Tsuga canadensis* (L.) Carr) and eastern white cedar (*Thuja occidentalis* L.). Red spruce (*Picea rubens* Sarg.) is a typical species of the Acadian Forest Region occurring in mixture with balsam fir and in mixed softwood-hardwood stands.

Tolerant hardwoods with minimal or no softwood content form major forest areas in southern Ontario and Quebec.

Although volumes of wood per unit area are, on the average, much smaller in eastern Canada than in the far western parts of the country, the area affected by above-natural acidic deposition contains, due to its vastness, more than one-third of the country's wood reserves. A major portion of this reserve consists of black and white spruces, the species which have given Canadian industries an advantage on the international newsprint market because of their high fibre quality.

According to the 1981 inventory data, the mean annual increment (MAI) (with an assumed rotation age of 80 years) in the affected area varied according to Forest Section (Rowe 1972) from 1.3 to 2.8 m^3 ha^{-1} (Bickerstaff et al. 1982). This includes the so-called operability-classes, 1 and 2 only, that are suitable for industrial use. This range is much below that of the Coast Forests of British Columbia, but it compares favorably with the national average of 1.7 m^3 ha^{-1}. For further comparison, the average MAI for the USA, Nordic countries and Central Europe, as estimated from FAO data (Bickerstaff et al. 1982), is 2.2, 1.8 and 5.3 m^3 ha^{-1}, respectively.

More than one-half of the current production within the area affected by above-natural acidic deposition in eastern Canada occurs within the Boreal Forest Region. According to Figure 1, the annual growth rate within the affected area of the Boreal zone corresponds to approximately 85 million m^3 of merchantable wood. Most of this, about 64 million m^3, is within the Province of Quebec. This is nearly as much as the annual forest growth of Sweden (Reed and Associates 1978).

The highest growth rate within the area receiving above-natural acidic deposition is shown for the Boreal Forest Section in New Brunswick. The forest lands of this province, which comprise about 6.75% of the total forest lands in the area affected by acidic deposition, contribute about 8% to the total annual production. Forest lands of Newfoundland-Labrador, having the lowest productivity, comprise about 5.8% of all forest lands in the affected area, but contribute only about 4% to the total annual production.

The total annual production of the entire area with above-natural acid deposition in eastern Canada is approximately 146 million m^3. This amount is comparable to the annual forest growth of all Scandinavian countries combined.

There are strong reasons to believe that at present Canadian forests produce far below the potential set by climate and soils. The main reasons for this are inferior growing stock, having resulted from local over-utilization and improper harvesting techniques, and the lack of species and stand-density control over significant portions of the forest land. An impression of the potential of the common cover-types to produce under average site conditions can be obtained from growth measurements. These have been made on adequately stocked experimental plots, carefully selected for fertilization studies across the provinces (Krause 1981; Krause et al. 1982; van Nostrand 1979). Information in Table 1 suggests that present rates of average production for a given Forest Section could, with appropriate management input, possibly be increased by a factor of two or more.

Two provinces, Ontario and New Brunswick, have embarked on new forest management programs in which renewable tenure agreements between governments and industries provide incentives for the latter to invest in publicly owned land in order to improve growing stock and future yields (Anon. 1980; Armson et al. 1980). In New Brunswick, for example, long-range projections are based on an assumed average yield of 210 m^3 ha^{-1} at a rotation age of 50 years from forests improved by planting or spacing.[1] This corresponds to a MAI of 4.2 m^3 ha^{-1}, which is more than double the present rate of production in the province. A question important to landowners and tenants is whether increased management inputs will be negated by continuing acidic deposition.

The pattern of forest ownership in eastern Canada varies with the provinces. In Ontario and Quebec, about 90% of the productive forest land is invested in the Crown. The remaining land is industrial freehold or in small private holdings, with the latter being the more common form of private ownership in Quebec. The productive forest land of Newfoundland and Labrador is controlled entirely by the Crown. In contrast, private ownership predominates in the Maritimes. In Nova Scotia, where public ownership comprises only one-fourth of all productive forest lands, the privately owned land is mainly in small holdings of less than 400 ha. In New Brunswick, non-industrial forest lands, i.e., private woodlots, comprise 30% of the total forest resource.

Possible losses from reduced forest growth in the areas with acidic deposition would be suffered collectively by the people in the provinces of Ontario, Quebec and Newfoundland, but predominantly by private individuals and corporations in the Maritime provinces. How imminent is the danger? The answer depends, besides on the rate of acidic deposition, on the ability of soils and bedrock to neutralize incoming pollutants.

Soils and Their Ability to Neutralize Acidic Pollutants

In the impact assessment under the Memorandum of Intent on Transboundary Air Pollution, signed by the governments of the United States and Canada (Bangay and Riordan 1982), soils and bedrock within the affected area have been rated with respect to their ability to neutralize the effects of acidic deposition. On the Canadian side, the rating of soils was based on depth, texture and the geologic origin of the parent material. Accordingly, the Boreal zone in general, and in Quebec in particular, is characterized by soils of "low" ability to neutralize acidic deposition. This is not surprising, as most of the soils have developed in shallow regolith derived from the granitic formations of the Canadian Shield (Douglas 1970). There are enclaves of varying size with medium or high neutralizing ability. These have soils derived from lacustrine deposits with a calcium carbonate horizon present at a depth determined by the amount of mean annual precipitation.

Soils of the Boreal Region, except those derived from lacustrine deposits, belong to the Podzolic Order (Clayton et al. 1977). Besides their high acidity and low degree of base saturation, such soils exhibit an additional feature of interest in connection with acidic deposition. This is the illuvial horizon with its accumulation of hydrated oxides of iron (Fe) and aluminum (Al). These substances adsorb much of the incoming SO_4^{2-}, while leading to a gradual decrease in soil pH and an increasing solubilization of Al (Norton 1976). It is the latter process that is believed to threaten root development and functioning (Ulrich 1980), hence forest productivity over the long term.

Coniferous growth on podzolic soils may be considered one of the forest ecosystems most sensitive to acidic deposition. Even though the accumulated hydrated oxides of Al may provide for some buffering against a further decrease in soil pH (Wiklander 1980), coniferous species are generally less efficient than hardwoods in base cation uptake and cycling. The latter are important processes counteracting acidic deposition. Furthermore, coniferous forests of the region have a strong tendency to be nitrogen deficient, which appears to be related to the slow organic matter decomposition in the originally acid soils. Fortunately, the Boreal zone is located at the periphery of the area with acid deposition.

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[1] T. Erdle, New Brunswick Department of Natural Resources, personal communication.

The Podzol soils extend southward into the mixedwood forests of the Great Lakes-St. Lawrence Region, including the Muskoka-Haliburton District of Ontario. Although this is in the zone of moderately heavy deposition, forest ecosystems may be somewhat less sensitive than farther north because of the larger hardwood component.

Podzols are gradually replaced by Brunisols and Gray Brown Luvisols. These are forest soils with a high base status. Having developed from calcareous or basic igneous rock materials and under predominantly deciduous forest, Brunisols and Luvisols have "medium" to "high" buffering ability for acidic pollutants. With hardwood cover, brunisolic and luvisolic soils probably represent the forest ecosystems with the lowest sensitivity to acidic deposition.

In the Maritime provinces, soils have developed from glacial drift over sedimentary and metamorphic rocks and over intrusive granites (Douglas 1970). Although some of the soils have been classified as Gray Luvisols (Clayton et al. 1977), they all reveal typical podzolic features including a low degree of base saturation and pronounced illuvial horizons with the accumulation of hydrated oxides of Fe and Al. Under the perhumid climate of the region, most of these soils have been acidified to one metre or greater depth. However, due to their medium and fine texture, soils over sedimentary rocks have been rated "medium" with respect to their ability to neutralize acidic pollutants. A comparatively small portion has been rated "high" because of the presence of calcareous parent materials.

Soils over intrusive igneous formations and contact metamorphic rocks, as in the New Brunswick Highlands and the Southern Uplands of Nova Scotia, tend to be shallower and coarser in texture than in adjacent areas. Their potential to neutralize acidic deposition has therefore been rated "low".

In the United States, soils representative of the area affected by acidic deposition fall into the Orders of Alfisols - the high base status forest soils covering the Great Lakes Region and being the counterpart to the Gray Brown Luvisols in Canada, the Spodosols - the counterpart of Podzols in Canada and covering the northern parts of New England and the Lake States, the Ultisols - the low base status forest soils common throughout the southeastern States, and the Inceptisols - the embryonic soils of the Appalachian Mountain ranges (Anon. 1975).

As in Canada, these soils have been rated with respect to their ability to neutralize acidic pollutants. Accordingly, two extensive regions have been identified as having a low neutralizing potential (Olson et al. 1982). These are the Spodosol-dominated New England region and the central portion of the Appalachian region where Inceptisols predominate.

The New England region, with deeper soils and a generally larger hardwood component, may be less sensitive than the Maritime provinces where major portions of adjacent land have actually been rated as having medium and high potentials for neutralizing acidic pollutants. Greater sensitivity is obviously displayed by coniferous forest x Inceptisol combinations at high elevations in the Appalachian ranges and in the Adirondacks of New York State. It must be emphasized that the occurrence of these types, unlike the Boreal Forest ecosystems of Canada, largely coincides with the zones of very heavy and heavy acidic deposition.

The general region dominated by Alfisols has been rated as having a moderate to high potential for neutralizing acidic pollutants. Forest ecosystems here, like those in the region of Gray Brown Luvisols and hardwoods in Canada, probably are not sensitive to acidic deposition. Also of low sensitivity to acidic deposition appear to be the forest ecosystems within the region dominated by Ultisols. Although Ultisols are characterized by low base status, their continuing weathering and the deep rooting and efficient nutrient cycling associated with hardwoods they support will most likely prevent short-term changes in cation reserves under present levels of acidic deposition (Richter et al. 1983). However, a different assessment may be necessary where softwoods are present instead of hardwoods.

Terrestrial Wildlife

The forests of eastern North America offer habitats for diverse wildlife populations. There is information in the literature to cause concern that many species, particularly the ungulates, may indirectly be affected by acidic deposition. Food sources may become contaminated with heavy metals, essential nutrient components may be lost from the food, and an overall reduction in food reserves could occur. Below are examples for each such possibility.

In an industrialized area of Poland, the antlers of roe deer (*Capreolus capreolus*) were shown to be contaminated with metals and reduced in size (Jop 1979). Deficiency of selenium (Se), an essential element in vertebrate nutrition, is not infrequent in livestock and has also been reported in several wildlife species (Stoszek et al. 1978). Availability of Se in soil and its uptake by plants depend on the pH of the soil. It is feared by some that continuing acidic deposition could sufficiently lower Se availability in forest soils and result in nutritional disorders in browsing species.

Diminishing food resources, resulting from acidic deposition, have been pointed out as a possible future constraint to the caribou (*Rangifer* sp.) herds in the Boreal forests and tundras of northeastern Canada. Lichens, the principal winter diet of caribou, have been proved sensitive to acidic deposition (Lechowicz 1981). The winter ranges of some of the largest caribou herds in North America are located within the area now affected by acidic deposition.

Aquatic Habitats

Acidic deposition via its action on soil and forest may have an indirect effect on water quality in streams and lakes. Of immediate concern is the possibility of a lowering of pH and an input of Al^{3+} into the aquatic habitats by run-off from acidified soils.

The sensitivity of fish to fluctuations in pH varies considerably, but certain species have failed to reproduce under laboratory conditions below pH 6 (Beamish 1976). With respect to Al, concentrations found to be lethal under laboratory conditions are not uncommon in headwater streams of areas with heavy and very heavy acidic deposition, as in the Adirondack Region of New York State (Driscoll 1980), the Great Smoky Mountains National Park, USA (Hermann and Baron 1980) and the Muskoka-Haliburton Area of Ontario.

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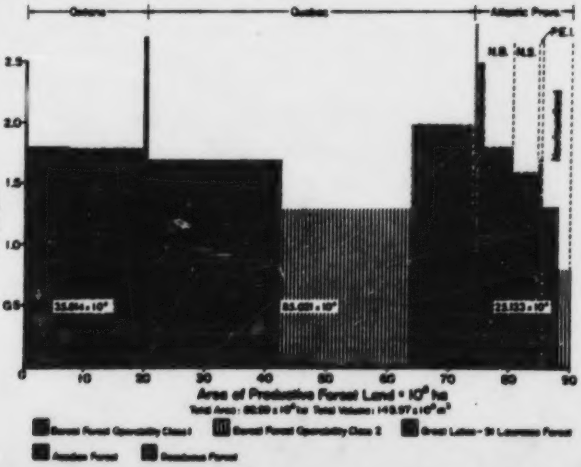
DISCUSSION

Question:	What is the conversion factor for millimoles (mmol) SO_4 m^{-2} yr^{-1} to kg SO_4 ha^{-1} yr^{-1}?
Answer:	The factor is about one.
Question:	How many millimoles (mmol) of hydrogen m^{-2} yr^{-1} did you consider heavy and very heavy deposition?
Answer:	Most people use SO_4^{2-} deposition to make this classification. Less than 20 mmol SO_4^{2-} m^{-2} yr^{-1} is considered light, 20 to 40 moderately heavy and greater than 40 is heavy deposition. A larger than 40 mmol SO_4^{2-} m^{-2} yr^{-1} deposition rate roughly corresponds to larger than 80 mmol H^+ m^{-2} yr^{-1} deposition. I have considered 40 to 80 mmol H^+ m^{-2} yr^{-1} as moderately heavy to heavy deposition and less than 40 mmol H^+ m^{-2} yr^{-1} as light deposition.
Question:	In boreal forest soils we frequently find layers of soil that reduce or prevent root development or deep root development and hence influence the cation uptake from deeper portions of the soil. Could you comment on this in relation to acidification?
Answer:	This reduces the input of base cations into nutrient cycles and results in naturally faster acidification of the soil surface layer. It is a condition that increases, in my view, the sensitivity of soils to acidic deposition.



A Forest Industry Perspective on Acid Deposition

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Good morning and thank you for the opportunity to speak at this Conference on Acid Rain and Forest Resources. The progress notes explain the background for the conference, stating that it is timely to take stock of our present state of scientific understanding, to recognize the high profile of the understanding known in an objective way. The United States forest products industry, together with the Canadian industry, very strongly support these goals. The economic health of our industry depends on abundant wood and low-cost energy. If these are threatened, then our industry is threatened. We look to this conference to provide sound science to help guide what we should do regarding our forests.

Our industry is an important part of the United States economy. In 1982, a recession year, the total production of paper and paperboard was 59.5 million tons, about the same weight as of manufactured steel products. Lumber production was 27 billion board feet (65 million m^3). The total value of shipments of these forest products, including their converted products, approximated 120 billion dollars.

Employment in the primary and converting operations totalled 1 275 000 people. In 1981, purchased energy consumption by the paper and paperboard industry was 10% of the total purchased by all manufacturing industry. Obviously, an industry with so much at stake needs sound technical information for its decisions. An example of the importance of such information involves siting of paper mills. Paper mills are particularly capital intensive, and once in place are captives of their geography. They depend on a very long and continuing supply of reasonable cost wood to survive economically. If acid rain damaged that supply, then the mills could fail and jobs would be lost.

Clearly, our industry can and should be a source of facts on the effects of acid deposition on the forest to assure our own survival. To that end, the industry, under the auspices of the American Paper Institute and the National Forest Products Association, with technical assistance from the National Council for Air and Stream Improvement, has enlisted the fifty largest forest industry companies in the United States to develop information on whether they believe their forests are being influenced by acid rain and what that influence might be. This program is now under way. In addition, the industry is supporting work on measurement of acid deposition rates, as well as defining the sensitivity of land over time to acidic inputs.

Our industry realizes that acid deposition and its presumed damage to the environment are very emotional issues, particularly in the public's mind, which receives very little well-organized and balanced information. Unfortunately, politics is also outrunning science. There are today in the United States Congress bills advocating reduction of emissions of SO_2 by 10-12 million tons per year by the early 1990s at an estimated cost of these reductions of 5 to 7 billion dollars per year. Increasing pressure is being mounted on the Congress by environmental groups, the media, and a poorly informed public to enact a bill this year spurred on by growing claims of harm to the environment. To cite an example, the New England River Basins Commission, in 1982, in a report to New England governors and eastern Canadian premiers, estimated that acid deposition caused 250 to 500 million dollars per year damage to the environment in the northeastern United States. Of this loss, 80 to 400 million dollars damage was asserted to be losses to the lumber and paper industries. The report went on to say that the losses were understated and concluded that they may be as much as 2.5 billion dollars per year. However, our industry does not know of such losses. Nevertheless, factually unsubstantiated assertions do get made.

Many scientists doing work in this field of acid deposition say that there is a very serious question as to whether acid rain has a significant effect on the forest and waters. There are scientists who hold that acidification is largely a natural consequence of forest growth and decomposition of forest litter; that elimination of acid deposition would raise pH of waters by less than a tenth of a pH unit, a negligible amount, and that this deposition has little effect on the forest. These scientists, many of them soil geologists and soil chemists, provide data that point to natural processes in the forest which create 5 to 10 times the amount of acid deposited from the atmosphere in areas such as southern Scandinavia or the Adirondacks, or New England, or Canada. They point out that soil humus, which is very acid, solubilized metal ions such as calcium and aluminum and that this action occurs in granitic regions such as the northeastern United States, Canada, and Scandinavia. The cool moist conditions of these regions favor the accumulation of the acidic organic humus. If these scientists are correct, and their data appear compelling, then excessive soluble aluminum, considered to be detrimental to trees and fish, is largely the result of natural processes and does not depend on man-made sources.

We in the forest products industry need to know whether natural acidification or acid rain is controlling forest growth. There is a body of information that clearly shows that surface run-off through humus can be very low in pH, reaching as low as 3.2 pH units in conifer areas, as that this acidification or run-off is the "normal tendency of ecosystems on base-poor substrata." Furthermore, there is evidence that land-use changes which lead to re-establishment of forest, particularly conifers, contribute to acidification of waters which were at one time far less acidic. This re-acidification has been suggested as a cause for declines in fish population. This does not deny that in a few very special situations small bodies of water at high elevations may be acidified from man-made sources, and special treatment of those waters may be desirable to mitigate the effect.

Some scientists attribute the die-back of red spruce in New England to acid rain, suggesting that an increase in acid deposition in recent decades is responsible; but historical data show episodes of red spruce die-back in the last century. Recent work has correlated this die-back to extreme drought, which drastically stressed the trees, particularly at higher elevations where the soil is thin. Apparently, scientists are not yet agreed on this die-back, but differences among scientists are to be expected since that data are limited and conflicting. Again, we need sound science to resolve these differences to guide our industry's action as may be appropriate.

The forest production industry is concerned about premature enactment of legislation to reduce emissions of the precursors of acid rain. The industry believes there is real uncertainty that any significant benefit to the environment would result from the very high costs which the public would ultimately pay. You are right in stating that "those in government, industry, and elsewhere, responsible for the well-being of the forest resource, or dependent on it for socio-economic values, have a right to look to the specialist for informed and clear analysis." The industry is concerned because the public is not aware that scientists are divided on what the real effects of acid rain are. The public is not aware that significant doubts exist about whether acid rain is the prime cause of environmental acidification. The pubic is barraged by assertions that reduction of SO_2 emissions, as is now being proposed in the United States, Canada and Europe, will correct a condition of damage to the environment. They believe acidification is of only recent origin and caused largely by acid emissions rather than primarily by natural processes of long standing.

We have an obligation to communicate both sides of the controversy to everyone, public, media, and legislators alike, to assure sound decisions.

Let me close with a quote of Bertrand Russell, the eminent philosopher, from his "Sceptical Essays":

The scepticism that I advocate amounts only to this:

> That when the experts are agreed, the opposite opinion cannot be held to be certain.
> That when they are not agreed, no opinion can be regarded as certain by a non-expert.
> That when they all hold no sufficient ground for a positive exist, the ordinary man would do well to suspend his judgement.

DISCUSSION

Question: If the US paper industry uses 10% of all the energy purchased, what is the fraction of total SO_2 emissions that can be attributed to the industry?

Answer: The figure, I believe, is well under 2%.

Question: Assuming acid deposition is reducing forest growth, say by 2 to 5% a year, would your company be more affected by this or by implementing controls on emissions?

Answer: I cannot compute in my head what the economic effects of one versus the other would be because I do not know what the costs of controls would be. If, however, the implication of the question is "Are you against controls?" the answer is that our company's health depends on have a continuing low-cost source of wood. If this is threatened than we would support controls on acid deposition. We need raw materials. At present we do not know that supplies are affected and until we know that controls are likely to benefit supplies, we advocate holding off

Invited Banquet Address
Forest Decline in Central Europe — Occurrence and Possible Causes

Peter Schütt
University of Munich
Federal Republic of Germany

ABSTRACT

Although the air-pollution damage to European forests that occurs near strong point-sources of emission has been known for many decades, regional forest decline — called "Waldsterben" in German-speaking countries — is a new and recent phenomenon, developing very rapidly in Central Europe since the 1980s.

Some North American forest scientists are familiar with this phenomenon, and some have visited Central European forests to see the problem first-hand; others have read the few available English-language accounts in the scientific literature, which up to now have tended to emphasize particular hypotheses or explanations of the malaise.

In this Address, a more rounded treatment of the topic is presented for North Americans. The different types of symptoms of decline are described and illustrated, the progression of the disease within the past few years is documented, and the main hypotheses for decline are outlined in an objective way, without any one theory being favoured exclusively over all others.

"Waldsterben" had occurred from time to time in silver fir (*Abies alba*), but its apparent spread to Norway spruce (*Picea abies*) in the late 1970s has been alarming, because this species makes up 40% of the forest cover in West Germany. Pine (*Pinus sylvestris*) has since become affected, followed by beech (*Fagus sylvatica*). In all cases, older trees on higher slopes have first exhibited decline, showing unusual foliar symptoms with branch loss or necrosis.

Of the several hypotheses proposed, the soil acidification/aluminum toxicity syndrome is probably the best known in North America, the idea being that acid deposition has intensified soil acidity to the point that the increased amounts of soil-aluminum mobilized kill tree rootlets. A second hypothesis sees acid deposition as having accelerated the loss of magnesium in foliage and soils, leading to the visible symptoms of chlorosis arising from magnesium deficiency. Related to this is the theory of excess nitrogen, again caused by acid deposition and bringing about nutritional imbalances and reduced hardiness. A somewhat different hypothesis involves harmful concentrations of ozone, which occur during dry hot summers at higher elevations when there is also likely to be a water-deficiency stress. Particularly attractive is the hypothesis of general stress, where a number of adverse environmental factors combine to disturb a tree's metabolism and photosynthetic efficiency. The tree succumbs to one or other adverse factors because there has been a general lowering of resilience.

Of considerable challenge is the way Waldsterben is seen over a wide range of tree species, regional climates and soil conditions. It is strongly believed that air pollution is an important component to the problem.

TECHNICAL SESSION I
POLLUTANT DEPOSITION TO FOREST ECOSYSTEMS

Wet Deposition to Forests

Dr. P.W. Summers
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ABSTRACT

The subject of wet deposition is presented in the context of the observed global distribution of precipitation chemistry and atmospheric processes. It is related to the natural and man-made sources of predominating chemical species. The development of sampling techniques and observing networks is summarized, and the important considerations of sampler location, time resolution, continuity of records and sources of error are discussed.

The main emphasis is on regions of heavy wet deposition, caused by man-made sources in eastern North America and Europe. Both spatial and temporal variations of deposition for the major ions (H^+, SO_4^{2-}, NO_3^-, NH_4^+, Ca_2^+, Mg_2^+) and heavy metals (Pb, Cd, Cu, V, etc. where available) are presented. The relationship between deposition patterns, meteorological and climatic factors and forest distribution is compared and contrasted between North America and Europe, in terms of events (short episodes of highly acidic deposition), seasonal variations (with special attention to snowpack accumulation) and longer-term trends.

Finally, the significance of a recently recognized form of wet deposition by fog and low cloud, especially on elevated forests, is discussed.

INTRODUCTION

The deposition of chemical species onto the Earth's surface is the end product of a long and complex chain of physical and chemical processes in the atmosphere. This chain has been discussed in detail in the comprehensive documents produced by the Working Groups established under the United States-Canada Memorandum of Intent on Transboundary Air Pollution (MOI 1982a, MOI 1982b) and summarized by Summers (1982). The various processes in the atmospheric emission-deposition cycle are illustrated schematically in Fig. 1. The long-range transport models used to simulate this cycle numerically, which attempt to produce quantitative relationships between emissions and deposition, have been summarized by Young (1982). Atmospheric deposition is, of course, a major input to the even more complex chain of physical/chemical/biological processes that take place in the land-water system, with that portion of the latter chain having implications for the forest ecosystem being the theme for this Conference.

Atmospheric deposition can be separated into two quite distinct processes — wet deposition and dry deposition — although in the case of forests, there can be important interactions between the two. Dry deposition is dealt with in detail in the next paper, but before leaving this topic, it is useful to consider in general the similarities and differences between the two processes and their relative contributions to total deposition.

DEPOSITION PROCESSES

Detailed reviews of dry- and wet-deposition mechanisms have been prepared by Garland (1978) and Hales (1978), and the important atmospheric processes for removal of the key sulfur and nitrogen species in particular are discussed in another MOI report (MOI 1982c).

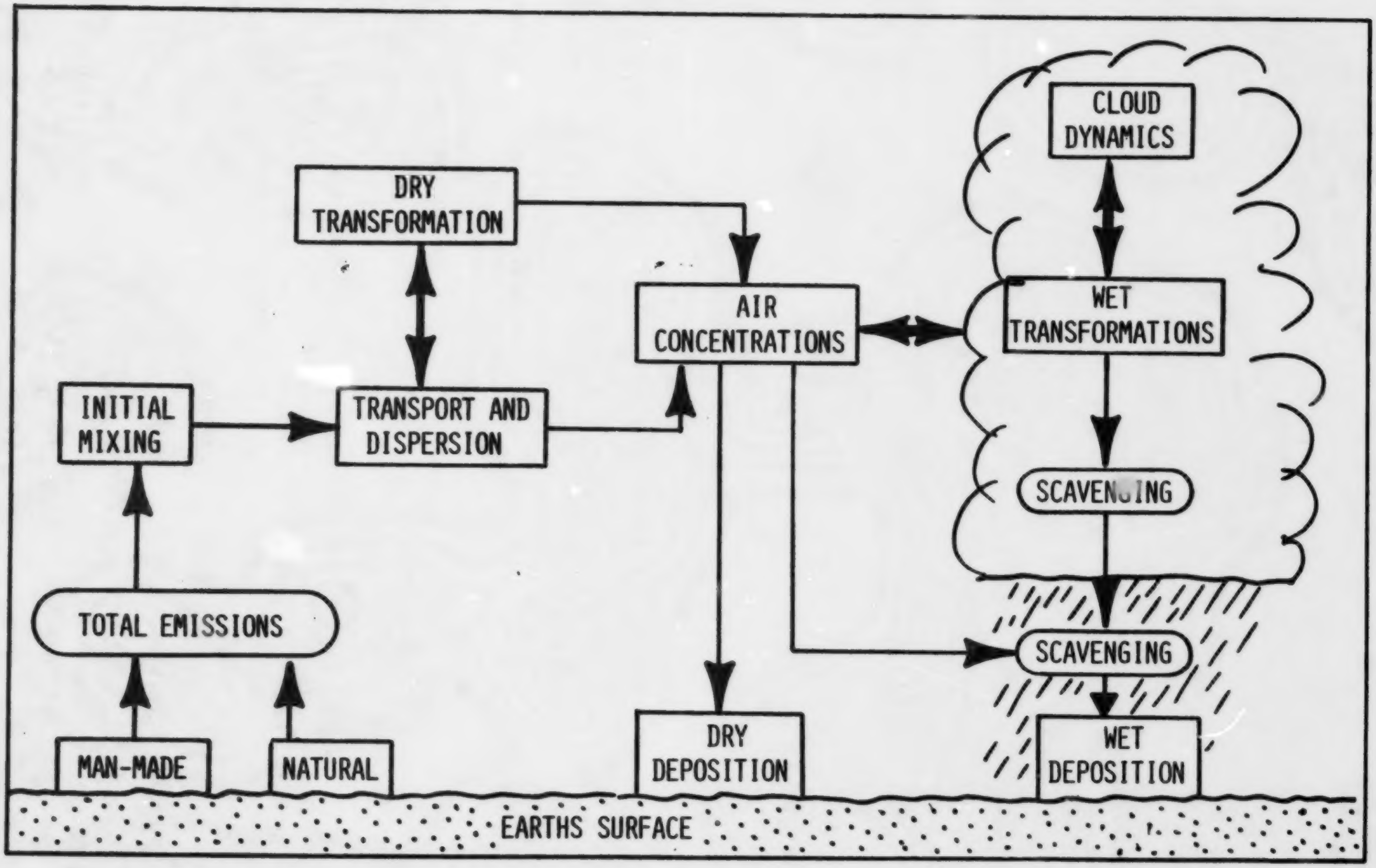

CLOUD DYNAMICS
DRY TRANSFORMATION
AIR CONCENTRATIONS
WET TRANSFORMATIONS
INITIAL MIXING
TRANSPORT AND DISPERSION
SCAVENGING
TOTAL EMISSIONS
SCAVENGING
MAN-MADE
NATURAL
DRY DEPOSITION
WET DEPOSITION
EARTHS SURFACE

Figure 1. The major components of the atmospheric emission-deposition cycle.

Dry Deposition

Dry deposition occurs during non-precipitating periods and is the accumulation on the Earth's surface of chemical species by any one or combination of the following mechanisms:

- settling, or sedimentation of particles,
- interception of particles on the surface roughness elements by impaction or by Brownian motion,
- surface chemical or biological reactions which result in a net uptake of gases by underlying surfaces.

Although methods for directly monitoring these mechanisms on a routine basis have not yet been developed, the dry deposition rate D_d can be estimated by use of the simple concept of a dry-deposition velocity (v_d) together with the monitored ambient concentrations (C_a) above the surface.

$$D_d = C_a v_d \tag{1}$$

The value of v_d can be determined experimentally over a variety of surfaces for a range of meteorological conditions.

Dry deposition does, of course, continue during precipitation, but is usually overwhelmed by the much larger wet-deposition rate.

Wet Deposition

Wet deposition occurs during periods of falling precipitation, which transports absorbed chemical species to the Earth's surface. The chemical species enter the falling hydrometeors by any one or combination of the following mechanisms:

- nucleation of cloud droplets by particles,
- absorption of gases by cloud droplets/crystals or falling precipitation,
- collection by various processes (e.g., diffusion, collision, etc.) of gases or particles into the cloud droplets/crystals or falling precipitation.

These processes are collectively referred to as scavenging, and the efficiency of these scavenging processes clearly determines the concentrations of the chemical species in falling precipitation. The rate of wet deposition (D_w) is, then, the product of the concentration (C_p) times the precipitation rate (P), with the latter parameter being analogous to the dry-deposition velocity described above:

$$D_w = C_p P \tag{2}$$

By setting up appropriate collectors, C_p can be monitored on a routine basis, and this is now being done by an increasing number of precipitation chemistry networks. The value of P can be obtained at these same sites and also from even denser networks of standard meteorological raingauges.

Another common formulation of wet deposition uses a scavenging ratio (W) defined as the concentration of a dissolved chemical species per unit mass of condensed water or ice (C_p), divided by the concentration of the same species (or its precursor) per unit mass of air (C_a).

$$W = \frac{C_p}{C_a} \tag{3}$$

Thus substituting in equation 2

$$D_w = C_a WP \tag{4}$$

where WP is now the term corresponding to the dry-deposition velocity.

The liquid water content (LWC) of clouds varies over the range 0.1 to 3.0 g m^{-3}. A typical value of LWC in a moderately precipitating cloud system is 1.0 g water (or ice) per m^3 of air (which weighs approximately 1 kg near ground level). Thus, if all of a given chemical species is scavenged by cloud drops, then there would be a magnification of the species concentration in the water by a factor of 10^3 over the original concentration in air. In this case, the scavenging ratio would be 1000. Data from locations where both precipitation and air chemistry have been simultaneously monitored at the ground in Europe and North America give values of W between 10 and a few thousand. Since there is a strong correlation between the precipitation rate (P) and the cloud LWC, LWC is implicitly accounted for in the parameterized formulation of wet deposition given by either equation 2 or 4.

Comparison of Wet and Dry Deposition Processes

As can be seen from equation 1 and 4 both wet and dry deposition rates are directly related to the ambient air concentrations. However, in eqation 1, C_a refers to the concentration just above the ground, whereas, in equation 2, C_a is strictly speaking the concentration at those altitudes where the scavenging is taking place. Because of the amplification effect mentioned above, wet deposition is a very efficient mechanism for removing material from the atmosphere; and $D_w >> D_d$. However, in mid-latitude temperate zones, it is raining only about 5% of the time, whereas dry deposition is a much more continuous process and is occurring most of the time between wet periods.

A very important distinction between wet and dry deposition is that the latter is highly dependent on the underlying surface. The value of v_d can vary over at least two orders of magnitude, with the lowest values occurring over flat, dry, frozen surfaces and the highest values over forests. On the other hand, the equivalent term for wet deposition WP is independent of the local underlying surface characteristics, although P is somewhat controlled by the larger-scale topographic features. In the case of taller vegetation, and especially forests, there is considerable modification of the precipitation chemistry between the top of the canopy and the ground. This interaction with the canopy is discussed in other papers, but for the purposes of the following discussion wet deposition will be defined as the flux of chemical species arriving at the *top* of the forest canopy in falling precipitation. Furthermore it will be taken to be equivalent to the flux measured by a collection gauge sited on the ground away from the direct influence of any obstructions.

Relative Importance of Wet and Dry Deposition

At the present time, only wet deposition is being monitored on a routine basis over large areas. Dry deposition of sulfur is being estimated at a few research sites and from a small number of stations routinely monitoring ambient concentrations of SO_2 and SO_4^{2-}. It is, therefore, impossible to get a precise measurement of the ratio of wet/dry deposition anywhere, but some estimates can be calculated that at least give a useful indication of the relative magnitudes. Three examples are given — two using the gross budget approach and one using point observations.

Gross Budget

Several global sulfur budgets were developed in the 1970s, and from the estimates for wet or dry deposition (Cullis and Hirschler 1980), the wet/dry ratio ranges about unity. The best estimate indicates that on a global basis wet deposition accounts for 58%, and dry deposition 42%, of the total deposition of sulfur.

A regional budget prepared for eastern North America (Galloway and Whelpdale 1980) estimates that the ratio of wet to dry deposition of sulfur is 2.5 for eastern Canada, and for the eastern United States, 0.85.

Single Stations

In 1979, a small network (APN) of stations was set up in eastern Canada to monitor precipitation on an event basis and to obtain 24-hour filter pack measurements of ambient SO_2 and SO_4^{2-}. Using the best estimate of deposition velocity, and taking into account the underlying surface and season, monthly dry deposition fluxes were estimated for each site (Barrie et al. 1984). The first year of data from 1979 showed that at Long Point, on the north shore of Lake Erie, close to large emission sources, the wet and dry deposition fluxes of sulfur were approximately equal. There was a tendency for wet to be greater than dry in the summer and vice versa in the winter. At Kenora, in northwest Ontario well removed from any large emissions, wet deposition (although much smaller than at Long Point) exceeded dry by an order of magnitude in some months, but the two were approximately equal in the winter months.

Some general patterns of dry and wet deposition fluxes are emerging, but it is important to remember that the type of underlying surface (which strongly influences v_d), the precipitation amount (which is influenced by topography) and the distance from emission sources are all highly variable from receptor to receptor. Thus, when conducting detailed studies in any particular forest region it is essential to make measurements locally.

WET DEPOSITION MONITORING NETWORKS

In the Appendix to the MOI Report (1982b), 38 identified networks were listed. These break down into: 2 global, 3 European, 20 Canadian and 13 in the United States. However, there are great differences between these networks in terms of the number of stations (2 to 150), the geographical extent and station density, the instrumentation used, the period of operation, the continuity of sampling protocols, and the extent to which Quality Assurance Programs were carried out. All such differences make it difficult to directly compare data between networks, although it does appear that the key measurements related to acidity, i.e., SO_4^{2-}, NO_3^- and H^+, are the most reliable. The MOI Report (1982b) contains a complete description of the monitoring techniques used, together with a review of the available data bases for inorganic species, heavy metals and some organics.

In response to the problems mentioned above, there are now extensive efforts under way, both nationally and internationally, to improve the coordination between networks through the development of more uniform siting criteria and instrumentation. In particular, strict Quality Assurance Programs and network intercomparisons are now being instituted, so that the user will have greater confidence in the data sets produced by all networks.

The following section will contain some of the more important results obtained from wet-deposition monitoring in North America, Europe and globally, to give an indication of spatial and temporal variabilities.

WET DEPOSITION OBSERVATIONS

Spatial Variations

On the global scale, based on the World Meteorological Organization global monitoring network (CAPMoN), the pH of precipitation shows a very distinct pattern. This general pattern, with only slight variations, repeats itself every year (Georgii 1982), and has the following main features: large regions with low annual average pH (< 5.0) over eastern North America and western Europe, with regions of high annual average pH (> 6.0) over the dry continental interiors of North America and Asia. The denser continental and regional networks give more details of the patterns; these show that in both North America (Fig. 2) and Europe, the areas of lowest precipitation pH are located over and immediately downwind of the major source regions of acid-forming emissions of SO_2 and NO_x. Figs. 3 and 4 show the wet deposition patterns for SO_4^{2-} and NO_3^- for North America and indicate a high degree of spatial correlation with the H^+ deposition shown in Fig. 2. The other important chemical species for forest ecosystems is NH_4^+, and its annual deposition indicated in Fig. 5 shows a quite different pattern, with an elongated east to west maximum extending from the high plain states across the Great Lakes and down the St. Lawrence River. This deposition pattern appears to be associated with the strong agricultural sources of NH^3 from feed lots and extensive use of fertilizers. These maps were originally prepared for the MOI (MOI 1982b), and then modified after careful quality control of the data (Barrie and Hales 1984) to produce those shown here in Figs. 2-5.

Deposition of heavy metals in precipitation has not been extensively monitored, but was reviewed in the MOI Report (1982b). A summary of the available published data is given in Table 1. Some information on deposition of trace metals in the 1980/81 winter snowpack in the Eastern Canadian Shield is given by Barrie and Vet (1984).

Table 1. Summary of Observed Rates of Wet Deposition of Heavy Metals (Units: mg m^{-2} yr^{-1})

METAL	URBAN INDUSTRIAL	RURAL	REMOTE
Cd		0.1 - 15	5×10^{-4} - 1×10^{-3}
Cr	11	3.6	
Cu	50	2 - 5	2×10^{-2} - 2×10^{-1}
Fe	30	54	0.2
Pb	~100	2 - 25	~5×10^{-2}
Mn	~10	2 - 25	3×10^{-2} - 9×10^{-2}
Hg		0.3	4×10^{-2}
Ni	10 - 80	1 - 10	
V	~50		
Zn	20 - 300	4 - 50	10^{-1}

Temporal Variations

The Annual Average

In the previous section the annual deposition was discussed, which is perhaps the most important averaging time-scale for assessing long-term effects on soils and on forest ecosystems. The annual deposition for only 1 year (1980) is shown in Figs. 2-5. The general nature of these patterns is very consistent from year to year, at least over the last few years, although there are small fluctuations in detail. How these patterns have changed over the longer term (last 10-30 years) is a where the position is uncertain and omitted in regions of insufficient data. (Source: Barrie and Hales 1984).

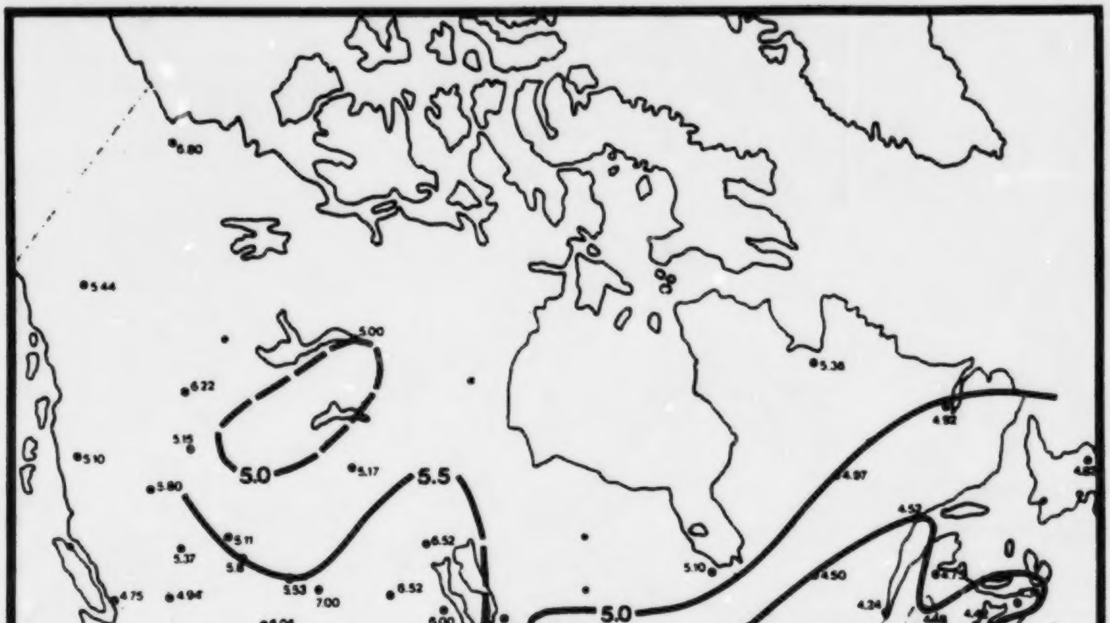
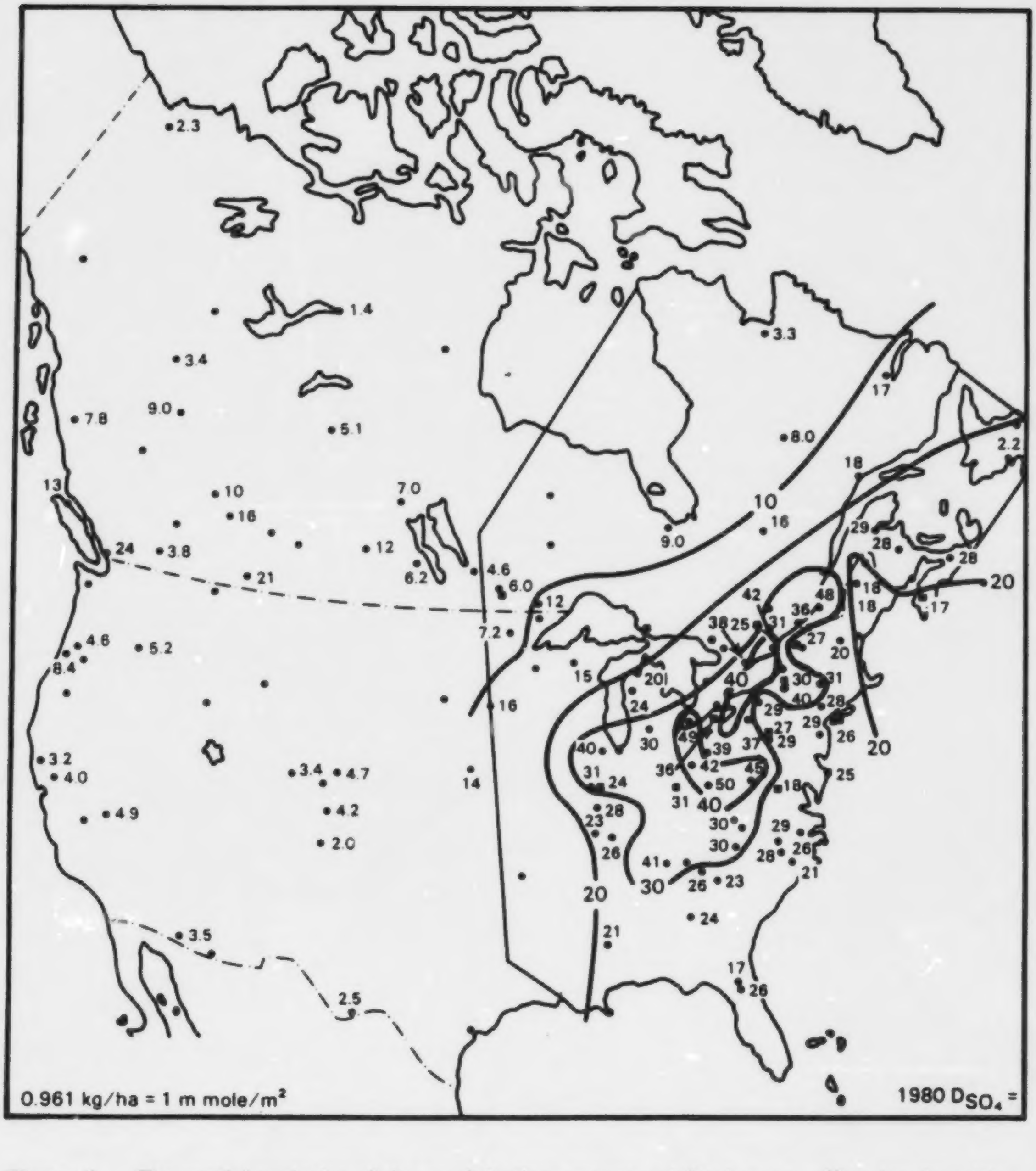

5.44
5.10
5.80
6.22
5.17
5.0
5.5
5.11
5.37
5.53
7.00
4.75
4.94
6.05
6.52
6.00
5.00
5.0
5.07
5.33
5.47
4.95
4.92
4.2
4.5
5.51
5.60
6.04
4.87
5.87
5.95
5.73
5.13
5.55
4.71
4.48
5.36
4.92
4.97
5.10
4.50
1980 pH

Figure 2. The spatial variation of the precipitation-amount weighted-mean pH over North America in 1980 compiled from several monitoring networks. Isopleths are dashed where the position is uncertain and omitted in regions of insufficient data. (Source: Barrie and Hales 1984).


0.961 kg/ha = 1 m mole/m²
1980 D SO₄ =
2.3
1.4
3.4
7.8
9.0
5.1
13
10
16
7.0
24
3.8
12
6.2
21
4.6
6.0
12
7.2
3.3
17
8.0
2.2
18
10
16
9.0
29
28
28
20
18
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42
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28
26
41
21
30
26
23
20
24
21
17
26
4.6
5.2
8.4
3.2
4.0
4.9
3.4
4.7
4.2
2.0
14
3.5
2.5

Figure 3. The spatial variation of the precipitation-amount weighted-mean sulfate ion deposition (mmol m-2) in North America for the year 1980. (Source: Barrie and Hales 1984).

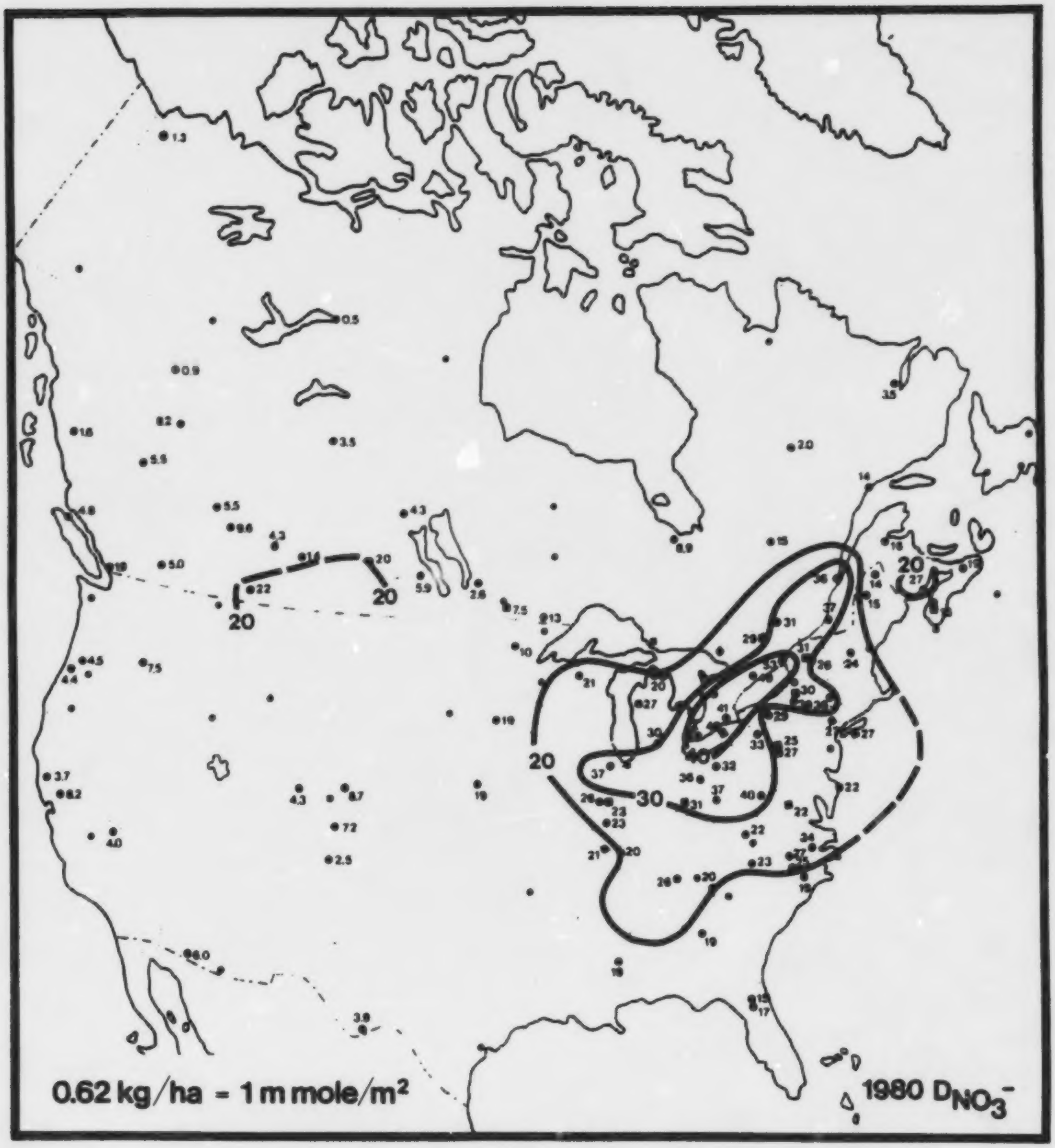
0.62 kg/ha = 1 m mole/m²
1980 D$_{NO_3^-}$
20
30
40
20
20
20
20

Figure 4. The spatial variation of the precipitation-amount weighted-mean nitrate ion deposition (mmol m^{-2}) in North America for the year 1980. (Source: Barrie and Hales 1984).

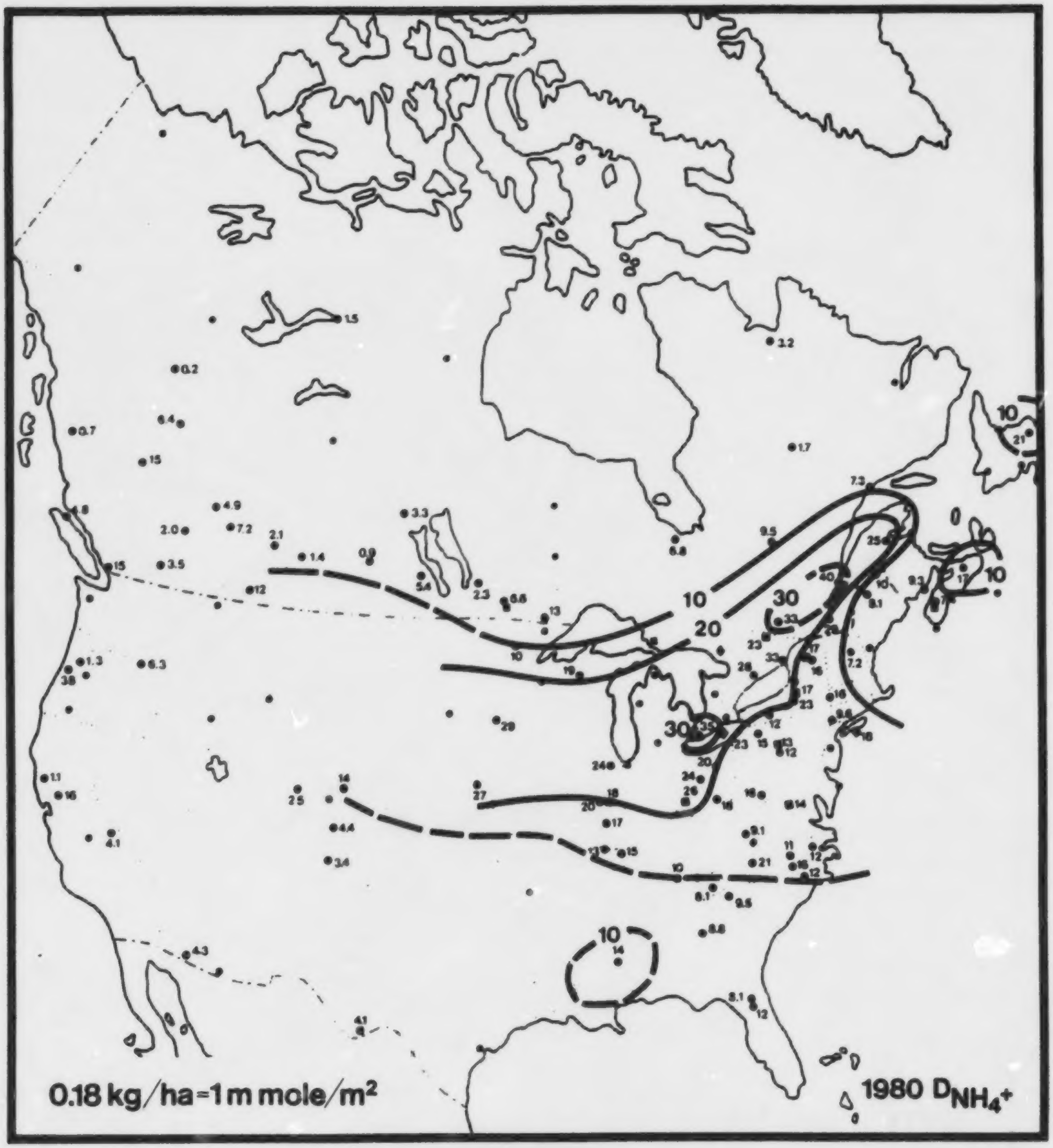
0.18 kg/ha=1 m mole/m²
1980 $D_{NH_4^+}$
10
20
30
30
10
10
10

Figure 5. The spatial variation of the precipitation-amount weighted-mean ammonium ion deposition (mmol m^{-2}) in North America for the year 1980. (Source: Barrie and Hales 1984).

matter of considerable controversy and will not be further discussed here. A comprehensive review of such trends has been carried out by Hidy et al. (1984).

Shorter time-scales are also important. Seasonal variation in deposition, especially the accumulation in the winter snowpack and the subsequent rapid run-off during the spring melt, have important ecological consequences. Direct damage to vegetation foliage has been linked to specific rain events when the pH is sufficiently low. These shorter period time variations in observed deposition will now be discussed.

Seasonal Variations

Individual stations in the CANSAP network have only a few years of record — barely enough to establish monthly averages. However, by grouping a few adjacent stations together into regions having similar climate, topography and agricultural practices, more stable averages can be generated (Barrie and Sirois 1982). Examples of the annual cycle for the deposition of key chemical species in some of the forested regions over a 6-year period are shown in Figs. 6-8, in units of kilograms per hectare per month. In the southern Canadian Shield, extending from Lake Huron to southwestern Quebec, the annual cycle of the eight major ions is illustrated in Fig. 6. This is a region having a very low annual average precipitation pH of between 4.2 and 4.4. However, there is a very strong annual cycle, with the H^+ deposition in summer period June to September being about twice that found in the winter period December through February. This acidity is due mainly to SO_4^{2-} and NO^{-3}, but these two species do not follow the same annual pattern. The NO^{-3} deposition tends to be higher in late winter/spring, reaching a maximum in April and low through the late summer. The SO_4^{2-} deposition shows a large, amplitude annual cycle, with a maximum through the warm months and a distinct minimum in mid-winter. In other words, the acidity of the summer rainfall is strongly dominated by SO_4^{2-}, but the winter snow accumulation, and hence the spring run-off, has a much higher relative NO^{-3} component.

Another important forest region is New Brunswick where the annual precipitation chemistry cycle is shown in Fig. 7. Here the H^+ deposition has a larger annual amplitude than in the Canadian Shield and follows the SO_4^{2-} cycle very closely. The NO^{-3} contribution to acidity is smaller and does not show a strong seasonal dependence. The effects of oceanic sea-salt (NaCl) are very strong during the stormy winter months, but are almost non-existent in the summer.

In the forests of the Pacific coast the H^+ deposition in precipitation is much lower than in the east, with a strong winter maximum (Fig. 8) associated with the heavier rainfall amounts. The SO_4^{2-} and NO^{-3} deposition both have a summer minimum, but neither shows a very strong seasonal variation. Again, the oceanic influence shows up in the sea-salt input of NaCl.

These three examples serve to show the strong regional differences and the systematic annual cycle of the inputs via wet deposition of the major chemical species to the forests across Canada.

Individual Events

In the previous sections data from stations in the CANSAP network, which collects monthly samples and therefore smooths out variations on a shorter time-scale. The Air and Precipitation Network (APN), consisting of a few stations at carefully selected rural sites, has been operating in Canada since 1977 and collects 24-hour rainfall samples. Observations at the sites in southern Ontario show that the H^+ from consecutive 24-hour rainfall events varies by one order of magnitude (Whelpdale and Barrie 1982), and that over an extended period of time about 20% of the total number of daily rain events account for 50% of the total deposition during the same period. An example of an

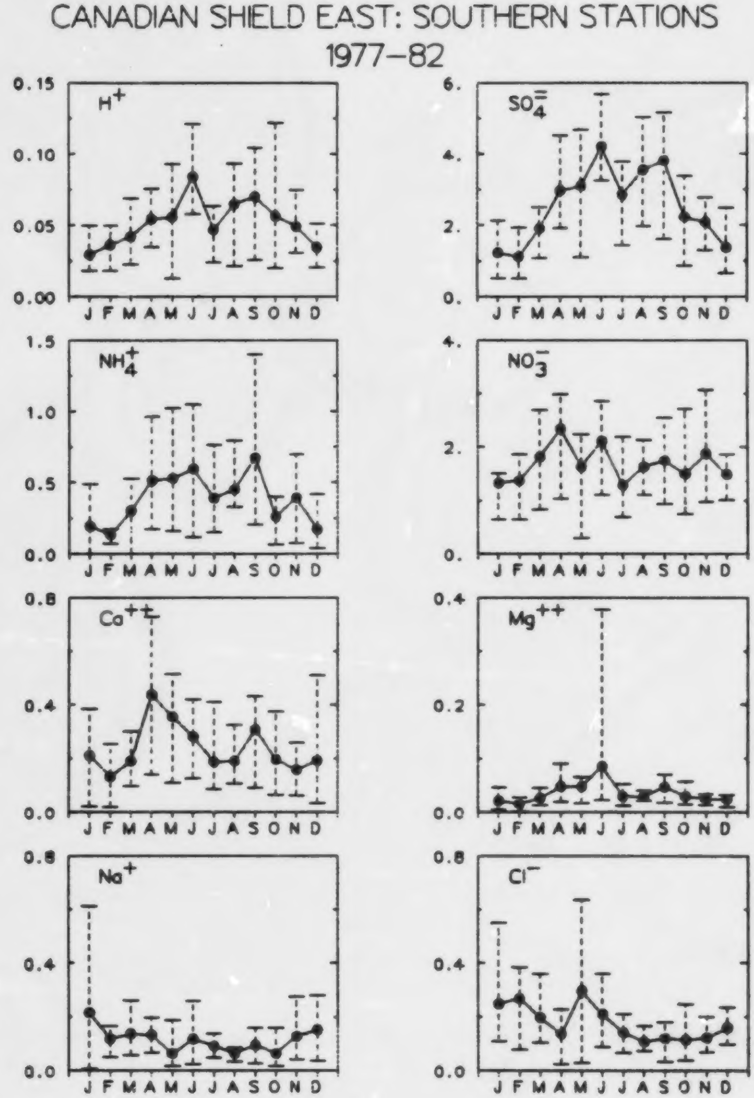

Figure 6. The annual cycle of the deposition (kg ha^{-1} mo^{-1}) of eight major ions found in precipitation in central Ontario and southwestern Quebec. The dot indicates the mean value, and the dashed vertical bars the total range over the 6-year period 1977-1982.

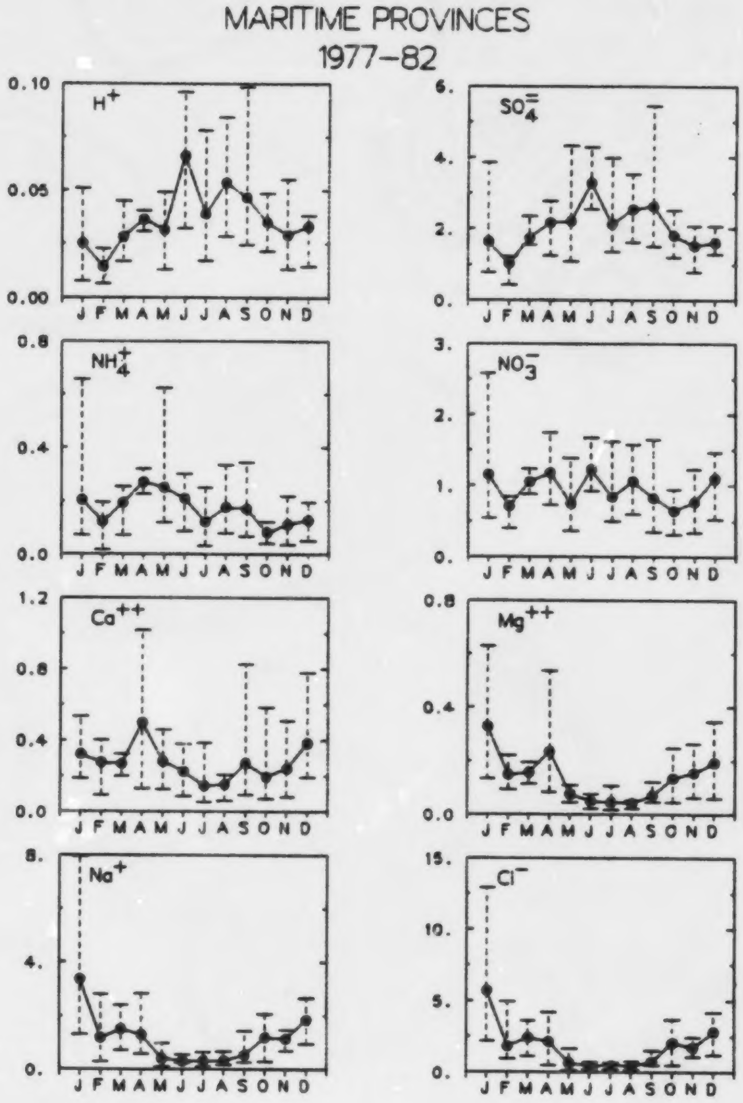

Figure 7. The annual cycle of the deposition (kg ha^{-1} mo^{-1}) of eight major ions found in precipitation in the Maritime Provinces. The dot indicates the mean value, and the dashed vertical bars the total range over the 6-year period 1977-1982.

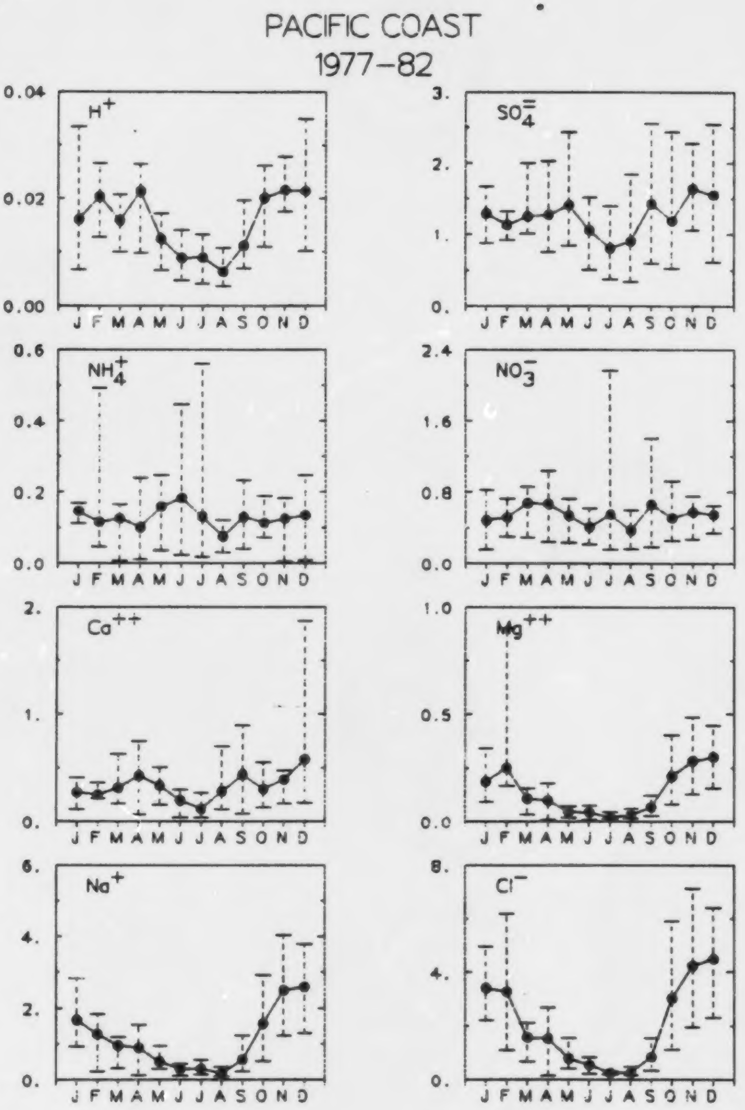

Figure 8. The annual cycle of the deposition (kg ha-1 mo-1) of eight major ions found in precipitation along the Pacific Coast region of B.C. The dot indicates the mean value, and the dashed vertical bars the total range over the 6-year period 1977- 1982.

exceptionally severe wet deposition episode is that occurring at Dorset, Ontario, from 28 August to 4 September 1981 (Kurtz et al. 1982), as summarized in Table 2. The daily average pH for the period ranged from 3.37 to 4.29 and was no doubt less for shorter time periods. During this 8-day period 12% of the 1981 total annual rainfall fell, but it contained 28% of the total sulfate wet-deposited in that year.

Variations occur over periods of minutes and hours, but not much information is available because of the requirement for special sequential sampling equipment and the high analysis costs. Within an event, such sampling shows that in polluted air masses the concentration of H^+ and most chemical species is high at the beginning with a strong general tendency to decrease with time (Raynor and Hayes 1978).

Table 2. Summary of the Intense Wet Deposition Event at Dorset, Ontario, 28 August to 4 September 1981

	Precipitation		Deposition, kg ha^{-1}	
Dates	Amount, mm	pH	SO_4^{2-}	NO_3^-
Aug. 28	20.0	3.77	1.73	0.52
29	6.8	3.37	1.35	0.47
30	7.8	3.64	0.90	0.33
31	4.4	4.14	0.16	0.06
Sept. 1	28.8	3.86	1.86	0.84
2	8.1	3.80	0.57	0.24
3	8.4	4.29	0.16	0.08
4	12.6	4.29	0.19	0.10
Episode Total	96.9		6.92	2.65
% of Annual 1981 Total	12%		28%	16%

WET DEPOSITION FROM FOG AND CLOUDS

A type of deposition which does not fit neatly into either of the two traditionally defined modes described earlier is that due to fogs or to low clouds. Deposition via this route had not been considered especially important until recent sampling of fogs and low clouds indicated high concentrations of acidic species leading to very low pH values.

Many of the forests in eastern North America and central Europe are on hilly or mountainous terrain and are frequently exposed to clouds or fog conditions (the distinction is really semantic, in that high-elevation fog is simply cloud that has reached ground level; both have similar physical and chemical properties). Trees act as efficient collectors of small water droplets in the air, and in some locations such collection is a substantial fraction of the total annual moisture input to the forest ecosystem. For example, the Boreal Forests of the Green Mountains in Vermont are above cloud-base for 800-2000 hours per year (Siccama 1974). This means that the forests are bathed in water droplets for 9 to 23% of the time, often for extended periods of several days. Such exposure is important in two ways. First, if the droplets are strongly acidic there is the potential for direct injury to the trees. Secondly, even if the airborne droplets are not acidic, after interception, they may dissolve acidic particulates deposited on the trees during a preceding dry-pollution episode.

Observations of Fog and Cloud Acidity

Observations of fog and cloud acidity are very limited, resulting from the initiatives of individual researchers rather than any systematic monitoring effort. A recent review of airborne cloud and precipitation chemistry measurements made over the past twenty years (Summers 1983) concluded that in general there is a tendency for the lowest pH to be found near cloud-base in the free atmosphere. Such low pH values are consistent with measurements made since 1977 atop Whiteface Mt., New York State, where most of the pH values for non-precipitating clouds range between 3.0 and 4.5 (Falconer and Falconer 1980), with the occasional value below 3.0. On an annual basis, the molar ratio of the SO_4^{2-} and NO^{-3} input to the acidity is close to unity. However, in the summer months SO_4^{2-} exceeds NO^{-3} most of the time, whereas in the winter months the reverse holds.

Another location where fog-chemistry sampling has been carried is out in the Los Angeles Basin (Hoffmann et al. 1982). The range of acidity is even lower than at Whiteface Mt., with the minimum pH of 2.25 recorded from only six events studied. However, in Los Angeles the dominant contributer to acidity is NO^{-3}.

In summary, mountain fogs or low cloud are now recognized as being a significant input to the water budget of high-elevation forests, and carry with them a substantial acid input of SO_4^{2-} and NO^{-3}.

COMPARISONS OF WET DEPOSITION INPUT TO FOREST CANOPY IN EUROPE AND EASTERN NORTH AMERICA

It is difficult to make precise comparisons of the total wet input to forests in various regions because inputs are very site specific. As indicated in the previous section the input from fogs and low cloud depends on the elevation. Rainfall amount is also strongly controlled by topography, but all the regional wet-deposition monitoring networks tend to have their stations at the more accessible lower elevations, hence probably underestimate the true chemical input by this mode. Comparisons can only be made, therefore, between the general regional input as shown in Table 3. There appears to be little difference in precipitation pH and concentrations of SO_4^{2-} and NO^{-3} between eastern Canada, New England and southern Sweden. However, the acidity is slightly higher in the Federal Republic of Germany, with a greater input of SO_4^{2-} and NO^{-3} ions. Differences between the inputs to these various forest regions arise from their elevation, total rain-flux, exposure to low-cloud fogs and synergistic effects with ambient pollutants such as ozone and SO_2. Unfortunately, the data do not exist at the moment to make such full comparisons.*

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* Since this paper was presented, a workshop sponsored by the US Environmental Protection Agency (EPA) and the National Science Foundation (NSF) was held in Albany, New York, 5-7 April 1984 to address this issue. A major recommendation was to set up monitoring sites with comparable instrumentation and sampling protocols at a series of high-elevation mountain sites in the eastern US, eastern Canada and central Europe to fully document the input to forests from the atmosphere.

Table 3. Comparison of Wet Deposition Inputs to Forest Canopy for Europe, Scandinaviá and Eastern North America

Forest Region	Annual Values		
		Range of Observed Concentrations	
	pH	Sulfate ($mg\ L^{-1}$)	Nitrate ($mg\ L^{-1}$)
Central Ontario Southern Quebec New Brunswick	4.2 - 4.4	2 - 4	1.25 - 2.5
New England	4.2 - 4.4	2 - 4	1.25 - 2.5
Federal Republic of Germany	4.1 - 4.3	6	3
Southern Sweden	4.3 - 4.5	2 - 4	1 - 3

CONCLUSIONS

Existing monitoring networks provide data on the pH and the species concentration in the precipitation input to the top of the forest canopy on an average regional basis over a wide range of time scales from annual down to daily events. These concentration fields of H^+, SO_4^{2-}, and NO^{-3} tend to be smooth when they are well removed (i.e., greater than a few 100 km) from major source-regions. However, because of the greater variability in precipitation amount, especially in the hilly and mountainous regions where most of the important forests are located, the fields in such locations of wet deposition input are more irregular and the amounts are very site specific.

A second, but less well-documented, influence on the variability of input to the forest canopy is due to the impact of fog and low clouds on elevated forests. In some areas this can be substantial and even exceed the input from precipitation. Again this input is very site specific.

The above indicates a clear need for more information on the wet chemical input to forests from both rainfall and cloud impact. In the meantime, caution must be used when interpolating between existing monitoring sites (usually at low elevation) to the intervening higher-elevation forest regions.

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GENERAL DISCUSSION

Question: It is estimated that sulfur from sea spray amounts to one-third of the total natural emissions. Should this source be neglected when looking at the acidity from SO_2 and H_2S emissions?

Answer: The point is that the sulfur component from sea salt is associated with sodium and calcium and, therefore, comes out as a neutral salt. Thus, in terms of contributing to the total acidity of precipitation, it really has no effect.

Question: To what extent are oceanic emissions returned to the ocean and how does this affect the per cent natural to per cent anthropogenic deposition in eastern North America?

Answer: Sea salt particles act as condensation nucleii and tend to get rained out in the coastal regions. Thus, any sea salt particles in the atmosphere in North America would contribute very little, except in a narrow strip along both the Pacific and Atlantic coasts. They have no real major impact on the deposition, once you get more than 50 to 100 km inland.

Question: Would you comment on the quantities of sulfate and nitrate deposited at present in eastern Canada?

Answer: Yes. The map showing deposition of sulfate was in m moles m^{-2} yr^{-1} and as pointed out earlier you multiply by 0.96, or essentially 1, to get the deposition in kg ha^{-1} yr^{-1}. Southern Ontario, southern Quebec and the Maritime provinces have greater than 20 kg ha^{-1} yr^{-1} of sulfate. For nitrate one has to multiply by 0.62 so that the deposition is considerably less in terms of kg ha^{-1} yr^{-1}. Southern Ontario would still be in the range of about 20 kg ha^{-1} yr^{-1}. In the Maritimes, Newfoundland and extreme eastern Quebec you are down to the order of 10 to 15 kg NO^{-3} ha^{-1} yr^{-1}.

Question: There are a variety of units used to measure concentration and deposition. To avoid confusion would it not be better to use either mole units/volume or mole units/area or mass S or N per unit volume or area? This would allow comparisons when deposition occurs in a variety of forms.

Answer: The problem is recognized, but there is no general agreement on the best units to use - each discipline seems to have its own preference. I must apologize that some of my maps varied in units but they were direct copies from the reports cited.

Dry Deposition and Ambient Concentrations

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ABSTRACT

The role of dry deposition in the acid rain problem is examined, particularly with regard to the forests of northeastern North America. Available data on ambient concentrations of the relevant atmospheric pollutants are reviewed and related qualitatively to the distribution of emission sources and to the prevailing meteorology. Cyclic seasonal and diurnal variations in concentrations are discussed, as well as the episodic nature of high pollution events.

Techniques for estimating dry deposition are briefly described. These include mass balance methods, dryfall collectors and surrogate surfaces, micrometeorological flux measurements, and methods of estimating depositions from ambient concentrations. The concept of a deposition velocity is considered in relation to the familiar resistance analogue for atmospheric fluxes within the surface layer. The dependence of deposition velocity on atmospheric parameters and surface characteristics is noted.

Finally, some estimates of dry deposition are presented. Results for particular experiments are given, as well as generalized regional patterns derived from the mean concentration fields. Direct measurements of deposition to forests have been relatively rare and so considerable uncertainty remains as to actual deposition rates to forests, especially for particulate deposition.

INTRODUCTION

Acid inputs to terrestrial ecosystems arise from two distinct processes, wet and dry deposition. Wet deposition refers to acid inputs due to material incorporated or dissolved in precipitation, either rain or snow, and which reaches the Earth's surface as a result of precipitation events. The transport by falling raindrops or snowflakes is easy to visualize, although the process which initially acidified the rain or snow may be complex. Measurement of wet deposition inputs, although requiring care to avoid external or internal chemical changes of the sample before analysis, is a fairly straightforward extension of procedures used for precipitation measurement.

In contrast, dry deposition is the direct scavenging or removal of material from the atmosphere by terrestrial surfaces without an intermediate precipitation phase. The material in the atmosphere may consist of suspended particulates or gaseous pollutants and may often be present only at very low concentrations. Concentrations of a few parts per billion in ambient air are not atypical away from source regions for even the main pollutants. Only the larger particles, that is particles with diameters in the order of tens of microns, have appreciable fall velocity, and for these the deposition process might be visualized as sedimentation. This process of large particle fall-out is a relatively efficient deposition mechanism, so efficient in fact that emitted large particles are virtually all deposited within a few tens of kilometers of the source and are not involved in long-range transport or in the acidification of more distant ecosystems. The sub-micron particles, which are the dominant size-class in the ambient atmosphere away from source regions, behave much as gaseous constituents. Deposition of these depends on a complex of interacting atmospheric, biological and chemical factors making direct measurement difficult.

Deposition rates for particular species are closely correlated with the ambient atmospheric concentrations of the species, consequently ambient concentrations are discussed later in this paper.

This apparent correlation has led to the widely used concept of a deposition velocity V_d where by definition:

$$V_d = \frac{\text{rate of deposition to a surface (mass per unit surface area)}}{\text{ambient atmospheric concentration (mass per unit volume)}}$$

Hence, V_d is a proportionality constant relating deposition to concentration and has the dimensions of a velocity. The concept of a deposition velocity is not meant to suggest an actual slow but steady downward velocity for individual particles or gas molecules. The deposition velocity represents an extremely simplified parameterization of the complex deposition process and can be expected to vary in both time and space in response to varying meteorological and surface conditions.

An appreciable proportion of the atmospheric input of acidifying material to terrestrial ecosystems may be the result of dry deposition. Dry deposition tends to be high near source regions where atmospheric concentrations are elevated and to decrease with distance from the source regions, reflecting the declining atmospheric concentrations due to dilution and removal processes. Wet deposition, on the other hand, tends to be maximized a considerable distance downwind of the source, due to the relatively slow conversion of the primary emitted pollutants into the secondary pollutants which dominate the acidification of precipitation. The relative importance of the two processes is often expressed as the wet-to-dry deposition ratio, which can be expected to increase with distance from source regions. This trend is illustrated in Figure 1 from Whelpdale and Galloway (1979). Drawing data from a number of sulfur budget studies, they show an inverse relationship between the wet-to-dry ratio and the mean emission rate of sulfur per unit area. In the highly industrialized areas of Central Europe, that is in regions of high sulfur emission rates, dry deposition may account for 70% of the total sulfur deposition. Averaged over eastern North America, wet and dry deposition are of comparable magnitude. In regions remote from industrial activity wet deposition becomes dominant, so that for eastern Canada (i.e., the Maritimes) and Norway, estimated dry deposition drops to 25% of the total sulfur input.

Clearly, dry deposition cannot be ignored when evaluating atmospheric inputs of acidifying material into ecosystems or watersheds. In this paper we provide an overview of the processes involved, as well as a brief examination of the probable concentration and deposition patterns over northeastern North America. Several other recent reviews on dry deposition, with extensive citations, are available for the interested reader, including those of Garland (1979), Sehmel (1980), Chamberlain (1983), and Hicks (1983).

Chemical Species

A wide variety of trace constituents may be present in the ambient atmosphere, but only a few of these are of significance to the acid deposition problem. These are summarized in Figure 2, taken from Ferguson and Machta (Fig. 2) 1982, which schematically illustrates the pathways from emission to deposition of the principal acidic species. These have been divided into three main categories, namely the sulfur pathway arising from anthropogenic emissions, largely as gaseous SO_2; the anthropogenic nitrogen pathway, largely due to NO emission; and the biogenic nitrogen pathway, characterized here as NH_3 emission. In all categories there is removal or deposition by both wet and dry processes. For sulfur, the main dry removal is by direct deposition of SO_2, but some deposition of the secondary sulfate aerosol may also occur, although the mechanism for the latter is inherently much less efficient. In the anthropogenic nitrogen pathway, dry deposition of the secondary gaseous pollutants, NO_2 and PAN (peroxyacetyl nitrate), may play a role, but the current viewpoint is that nitric acid deposition is the most important. The biogenic pathway is at present poorly quantified, but it is known that plant material can take up, as well as emit, NH_3; dry deposition of particulate NH_4^+ is also a possibility.

Considerably more information is available for the sulfur pathway than for the nitrogen pathways, particularly with regard to the dry deposition of SO_2. Gaseous deposition is in general better understood than particulate deposition, although the general pattern of sulfate aerosol formation has been delineated. A typical atmospheric particle size spectrum might look like Figure 3 (from Hicks 1983). Particles may initially form as Aitken nuclei from the oxidation of SO_2 to sulfate aerosol, and by other gas-to-particle conversions. These grow by coagulation to become particles in the size range of tenths of a micron to a few microns, but growth rates decline with decreasing mobility of the particles as they enlarge, so that there is typically a maximum in the particle spectrum below one micron. Windblown dust and industrial emission of coarse particles can result in another maximum around ten microns. Large soil-derived particles are usually neutralizing rather than acidic, and sedimentation plays a significant role in their removal. Particles currently of most concern for long-range transport and acid deposition are those in the accumulation mode. Most studies have shown deposition mechanisms to be relatively inefficient for particles in this size range, an aspect discussed in the next section. The possible impact of the relatively rare but more efficiently deposited super-micron particles has also to be taken into account.

Deposition Mechanisms

Several factors are known to influence rates of dry deposition. These are summarized in simplified form in Figure 4 (after Hicks 1983). Separate pathways are shown for gases and particles since different mechanisms may be involved. Conceptually in Figure 4, particles and gases originate at some airborne source remote from and unaffected by the receptor surface. Exchange between the source and the immediate environment of the receptor is due to turbulent transport by atmospheric eddies, that is, by aerodynamic factors. For large particles, gravitational settling is also important. The solid surface of a receptor presents a barrier to air movement. Consequently turbulent eddies do not penetrate right to the receptor surface, rather the receptor surface is sheathed by a thin quasi-laminar layer, the thickness of which may vary depending on receptor shape and orientation and on the intensity of the turbulent flow immediately above.

Gaseous pollutants cross this laminar sub-layer by molecular diffusion, whereas for small sub-micron particles the analogous process for crossing this layer is Brownian diffusion. Interception and inertial impaction contribute to the movement of larger particles across the surface layer in addition to Brownian motion. For particles greater than ten microns, gravitational settling becomes a dominating mechanism. The efficiency of the transport in the laminar sub-layer is highly dependent on the mass or size of the transported molecule or particles. Molecular diffusion and Brownian motion become less efficient as molecular weight or particle size increases, whereas interception, impaction, and gravitational settling of particles become more efficient deposition mechanisms as size increases, until particle bounce-off becomes significant. Plots of particle deposition velocity as a function of particle size (Figure 5) have a well-defined minimum at particle diameters between 0.1 and 1.0 microns, which is the size range where neither Brownian motion nor inertia-dependent mechanisms are very effective. The deposition velocities shown in Figure 5 are based on values determined by Chamberlain (1966) in wind tunnel studies. These results are similar to other wind tunnel studies and to the modeled deposition rates given in Sehmel (1980), but are not necessarily the same as deposition rates to natural outdoor surfaces. Other physical processes can also influence transport near the surface. These include Stefan flow for both particles and gases (a flow which arises from the addition or removal of material at the surface and is largely associated with the evaporative flux of water) and possibly phoretic effects for particles that, as yet, are ill-defined for atmospheric exchanges. Transport across the laminar sub-layer can be modified by the specific properties of the receptor, such as shape, orientation in the mean flow, smoothness, flexibility and motion (fluttering) due to the air flow.

The retention of either particles or gases depends on the surface characteristics, particularly for super-micron particles which are subject to bounce-off, or for gases which must be chemically retained by the surface. Surface waxiness, vestiture, exudates, chemical nature, wetness, and, for vegetation and gaseous uptake, stomatal opening may all be important. Net uptake may also be modified by the emission or re-entrainment of chemically related material.

The variety and complexity of the processes involved in the deposition pathway have precluded development, as yet, of quantitative models that deal effectively and explicitly with the physics and chemistry of the deposition process. However, various simplified models have been derived which can, in some instances, give reasonable estimates of deposition rates and their temporal and spatial variations. This is now discussed.

Resistance Analogues for Dry Deposition

Resistance analogues model atmospheric fluxes according to the flow of electric current, I, through a resistor, R, as given by Ohms law, V = RI, where V is the potential difference. The deposition velocity parameterization can be considered as a simple resistance analogue for deposition. The flux or current of material from the atmosphere, F_c, to the surface is assumed proportional to the driving force or potential difference given by atmospheric concentrations, C (which implies concentration at the receptor equals zero). The deposition velocity, V_d, is thus equivalent to an electrical conductance and

$$F_c = V_d C$$

This simple parameterization, however, is not very realistic physically and it is difficult to relate in a simple way temporal and spatial variations in V_d to specific processes. Considerable improvement can be achieved by slightly more complicated models, such as that given in Figure 6. This has proved very useful for evapotranspiration studies (Monteith 1973). The three basic processes shown in Figure 4 are each modeled by a separate resistance — r_a for aerodynamic transfer, r_b for laminar layer transfer, and r_c for surface-related properties. In contrast to simple electrical circuits, the resistances r_a, r_b and r_c are not constant, but considerable information on their variation with various environmental factors can be deduced from the similarity of pollutant transfer to the transport of momentum, heat and water vapor for which a considerable background of micrometeorological studies exists.

The aerodynamic term, r_a, reflects transport by turbulent eddies. This process can only be considered analogous to the flow of electrical current when averaged over appropriate time intervals. These have to be much larger than the scale of aerodynamic eddies, which fluctuate rapidly between upward and downward motions as a consequence of turbulent changes in vertical velocities. This is illustrated in Figures 7, 8, and 9, which are field measurements made during a "Dry Deposition Intercomparison Study" at Champaign, Illinois, during June, 1982 (Neumann et al. 1983). Figure 7 shows measured vertical components of the wind, w, and the concentrations of water vapor, ozone and atmospheric sulfur over a 1-minute interval near mid-day on a warm, sunny day in late June, all measured 4.5 m above a grass field. Large fluctuations occur on timescales of a second or less, but also apparent, particularly in the watervapor trace, are periodic eddies on time scales on the order of 10 seconds which represent recurring buoyant plumes, with maxima in water vapor concentrations (and minima in pollutant concentrations) tending to be associated with upward vertical velocities indicative of air parcels originating at the underlying surface. Also apparent in the watervapor trace are quiescent periods of relatively lower concentrations and small or zero vertical velocity, which are representative of conditions in the free atmosphere away from the surface. Instantaneous fluxes are given readily by the product of the instantaneous concentration and vertical velocity, and these total fluxes for the same period are shown in Figure 8. These fluxes are very large when compared to the net fluxes at the surface for either evaporation, the upward flux of water vapor, or deposition for ozone and atmospheric sulfur. When these instantaneous fluxes are averaged over periods of fifteen minutes or longer, the upward and downward fluxes tend to balance is each other, resulting in relatively small net fluxes. In micrometeorological work it has been useful to separate the mean and fluctuating components of atmospheric parameters to delineate the large disparity between instantaneous and net fluxes. The concentration C of an atmospheric component can be expressed as $C = C + C^1$ where C =

mean concentration, and C^1 = the fluctuating component about the mean ($C^1 = 0$ by definition). Similarly, the vertical velocity can be expressed as $W = W + W'$. The resulting equation for net flux, $F = WC$, becomes:

$$\begin{aligned} F &= (\overline{W} + W^1) \bullet (\overline{C} + C^1) \\ &= \overline{W} \bullet \overline{C} + \overline{W} \bullet \overline{C^1} + \overline{W^1} \bullet \overline{C} + \overline{W^1 \bullet C^1} \end{aligned}$$

noting that $W^1 = C^1 = 0$ by definition,

$$F = \overline{W} \bullet \overline{C} + \overline{W^1 \bullet C^1}$$

Assuming constant pressure P, W must be very nearly zero, otherwise air will be accumulating or depleting in the layer below the measuring height, so that in general, $W \bullet C$ is quite small. Actual values of W in the surface layer are too small to be measured directly but can be computed if the heat flux and water vapor flux are known (Webb et al. 1980). Typically, the flux is dominated by the term $W^1 \bullet C^1$, the so-called eddy flux. This eddy flux is also plotted in Figure 8 and appears almost as a zero axis for the total instantaneous flux traces. Its magnitude is less than 10% of that of the total instantaneous flux. The bulk of the variation in the total flux is due to the $W^1 \bullet C$ term which has a time average value of zero. Figure 9 shows the eddy-flux term plotted on a scale 10 times that of Figure 8. For the sulfur and ozone flux a dotted line has been added, giving the equivalent constant flux for $V_d = 1.0$ cm s^{-1}, a typical value of gaseous deposition. The intermittent nature of the eddy flux is readily apparent and it is notable that for the eddy flux of sulfur and ozone, in contrast to the total flux in Figure 8, upward W's contribute to a downward flux since they are associated with concentration minima or negative C^1. The peak-to-peak magnitude of the instantaneous eddy flux is nearly 10 times the mean flux. Hence for sulfur and ozone, the mean deposition is only about 1% of the peak-to-peak variations in instantaneous atmospheric fluxes at 4.5 m above the surface. The intermittent and turbulent nature of atmospheric transport is all concealed in the r_a term of the resistance model.

Semi-empirical relationships have been developed relating the r_a term to wind speed, surface roughness and thermal stability of the atmosphere (e.g., see Rosenberg et al. 1983). It has been convenient to define r_a as the resistance for momentum transfer or drag τ due to a mean wind, U, so that $r_a = \rho U/\tau$ where ρ = air density. Then, assuming a perfect source or sink at the surface, r_b becomes the additional resistance to transfer for scalar quantities such as heat, water vapor and air pollutants. It is attributed to the additional sink due to form drag for momentum, which is not available for the scalar quantities. Thom (1972) has shown r_b to be a function of the momentum flux and the relevant molecular diffusivities for gas-phase transfer, but similar relationships for r_b in particle transfer have yet to be verified.

The surface may act as a perfect sink (or source) for heat and for highly reactive pollutants, such as nitric acid, but for many substances it is necessary to introduce an additional surface resistance, r_c. Often for gaseous transfer to and from vegetation, r_c can be considered to be largely due to diffusion through the stomatal pores, hence inversely related to molecular diffusivities. More than one pathway may be involved; for example, cuticular and stomatal resistances acting in parallel for transpirational water losses. Where the various pathways are known and can be quantified, correspondingly more elaborate and meaningful resistance networks can be constructed; for example, the atmosphere plant-soil system shown in Figure 10 with separate pathways for plant and soil.

More elaborate multi-layer resistance models, which include intra-canopy transfers, have been constructed (Norman 1979). It is, however, important to remember that the resistance analogues are still an extreme simplification of complex turbulent transfers; environment-canopy interactions and extensions beyond what has been verified experimentally must be viewed with caution.

MEASUREMENT TECHNIQUES

Micrometeorological Methods

It is now apparent that transport mechanisms associated with dry deposition are considerably more complex and more difficult to quantify than the measurement of rainfall and perhaps snowfall. Several techniques have been used or proposed for dry deposition measurement and are summarized in Table 1 (after Hunt et al. 1981). Methods 1 to 4 can broadly be described as micrometeorological measurements, in that derived depositions are based on exacting measurements in the atmosphere above the surface of interest. Strictly speaking, surface deposition is not measured, but rather the net atmospheric flux at some height, typically 0.5 to 10 m, above the surface, which is assumed to be the surface flux. This can only be valid if the flux is constant from the surface up to the measuring height (flux divergence = 0). This requires a homogeneous surface in the vicinity of the measuring point and stretching some distance upwind so that the sensors are within the boundary layer in equilibrium with the surface. A general rule of thumb is an upwind fetch-to-height ratio of 100:1, provided that the change at the upwind boundary is not overly extreme.

The eddy correlation method is essentially a direct measurement of the eddy flux. Concentrations and vertical velocities must be sampled at a rate faster than fluctuations contributing to the flux (typically 5-10 Hz at 3 to 4 m), and data-handling systems must be capable of processing data acquired at such rates. Instantaneous products, WC, are computed and accumulated to give net fluxes over averaging periods typically 0.5 to 1 h. Eddy accumulation (Desjardin 1977; Neumann et al. 1983) is a variation on the eddy correlation method. A fast response sampling system substitutes for a fast response pollutant sensor. By sampling at a rate proportional to W, and by accumulating samples separately for W positive and W negative (e.g., on filters for particulates, or in teflon bags for gases), it is then possible, in principle, to compute the flux from the difference in material accumulated for the up and down samples. High relative accuracy rather than fast response becomes the limiting pollutant-sensor requirement. The eddy accumulation method has several attractive features but has yet to be proved for pollutant deposition study.

The gradient method relies on an assumed similarity of transport for a pollutant compared with another atmospheric component the eddy flux of which can be determined. The method has been widely used. In resistance notation the flux can be expressed as $F_c = (C_1 - C_2)/r_{1,2}$ where C_1 and C_2 are the mean concentrations of C at heights Z_1 and Z_2 respectively and $r_{1,2}$ is the aerodynamic resistance for C between these heights. If we consider another flux, for example flux heat H, and assume the same aerodynamic resistance $r_{1,2}$, then $H = \rho C_p (T_1 - T_2)/r_{1,2}$ where C_p = heat capacity of air at constant pressure, and T_1 and T_2 are mean temperatures at heights Z_1 and Z_2. Hence

$$F_C = \frac{H}{\rho C_p} \bullet (C_1 - C_2)/(T_1 - T_2)$$

The gradient method requires measurements of high relative accuracy at a minimum of two levels in the surface boundary layer and a method of determining the flux and gradient for some other atmospheric component. Fast time response is not required, as measurements must be averaged over minimum periods approaching one half hour in order for the flux-gradient relation to be valid. The method depends on the validity of the similarity assumption, which has usually proved adequate except very near or within vegetative canopies.

Table 1. Evaluation of various experimental methods to measure and parameterize dry deposition rates to forests

Method	Time Scale	Space Scale	Measured Substance	Technical Difficulty	Development Required	Relative Cost	Suitability for Parameterization	Monitoring Suitability	Comments
Eddy Correlation	Hour	Point	Gases Particles	High	Medium	High	High	Low	Development required for fast response sensors
Variance	Hour	Point	Gases Particles	Medium	Medium	Medium	Medium	Medium	As above
Concentration Gradient	Hour	Point	Gases Particles	Medium	Low	Medium	Medium	Low	Requires simultaneous measurements of heat flux
Eddy Accumulation	Hour	Point	Gases Particles	High	High	Medium	Medium	Low	Method under development
Dryfall Collectors	Week	Point	Particles	Low	Low	Low	Low	Low	Requires high degree of interpretation
Surrogate Surfaces	Day	Point	Particles	Medium	Medium	Medium	Low	Medium	As above
Surface Accumulation	Day-Week	Point	Particles	Medium	Medium	Medium	Low	Medium	Subject to interferences from leaching or fogs translocation and acid mists
Tracer	Hours-Weeks	Point	Gases Particles	Medium	Medium	Medium	Medium	Low	Radioactive tracers require special licenses and handling
Mass Budget	Week-Month	Areal	Total	High	Low	Low	Low	Low	Difficulty in meeting normal mass budget assumptions
Cuvettes or Chambers	Hour		Gases	Medium	Medium	Medium	Low	High	Extension to deposition rates difficult
Concentration	Hour	Point	Gases Particles	Medium	Medium	Medium	Low	High	Requires knowledge of deposition velocities

The final micrometeorological method given is the variance method. Experimental evidence (Wesley and Hicks 1978) and similarity theory (Tennekes 1973) support the hypothesis that flux is proportional to variance. Given the variance σ_c^2 of C, and the flux and variance of another component, say heat flux H and variance of temperature σ_T^2, variance method assumes $F_c = H/\rho C_p \bullet \sigma_c^2/\sigma_T^2$. The method requires fast-response, low-noise sensors, but relaxes the requirement of high relative accuracy as required by the gradient method, or necessarily for a W-sensor. Appropriate pollutant sensors have not, as yet, been developed and it is questionable whether the method will replace the eddy correlation method.

All micrometeorological techniques require relatively sophisticated on-site instrumentation that must be carefully calibrated and maintained. They are more suitable for limited parameterization studies rather than routine, long-term monitoring. They measure net atmospheric fluxes at some height above the surface, rather than deposition, and it is conceivable that at small deposition rates ($V_d < 0.05$) flux divergence may limit applicability (Slinn 1983).

Passive Collectors

Passive collectors have been extensively used for particulate deposition measurement and probably have been relatively successful for large particle deposition that is dominated by gravitational settling. In Table 1, we consider dry fall collectors, surrogate surfaces and surface accumulation to fit into this category. Dryfall collectors include various artificial surfaces and containers used to catch atmospheric particulates and have the characteristic that no attempt is made to model or simulate the natural surfaces of concern. Surrogate surfaces on the other hand are artificial surfaces made to physically resemble the natural deposition surfaces. Surface accumulation refers to measuring actual accumulation on the natural receptor surfaces. Of these three methods, dryfall collectors are the least satisfactory. Efficiency for a collector is intimately related to its surface characteristics, shape and exposure to the air flow. If these differ significantly from that of the natural receptor, then the material captured by the artificial collector can vary substantially from that collected by the natural receptor, quantitatively, qualitatively (e.g., size distribution of collected material), and temporally in a manner that is difficult to predict or calibrate. Surrogate surfaces attempt to minimize these differences by making the collector similar in form to the natural receptor, but since the similarity in design and exposure is seldom perfect, calibration and validation should still be performed. Surface accumulation by the actual receptors of concern, such as leaves or branches, can provide data on deposition if there are no translocation or removal processes, unrecognized or unaccountable chemical transformations, incomplete recovery of material in the analyses or other sources of the same material resulting in surface deposits, during the period between deposition and sample collection and analysis. For these reasons, leaf-washing experiments must be viewed with some caution, and deposits attributed to dry deposition may arise in part from wet deposition in acid fogs and mists.

Tracers

Very useful information on particle deposition has been obtained by studies using releases of radioactive tracers to measure uptake to vegetation (Chamberlain 1966; Owens and Powell 1974; Ibrahim et al. 1983). The success of these studies has been aided by unambiguous identification of deposited material, because it is radioactive, and the relatively short time interval required to achieve a measurable deposition. Surface accumulation studies have often only looked at selected sub-samples of complex surfaces, and, if total deposition is the desired output, there may be a problem extrapolating results, for example, when estimating dry deposition to a forest based on measurements for a few branches.

Naturally occurring radioactivity can also be used as a tracer in some instances. For sulfur deposition, variations in the isotopic ratio of ^{34}S to ^{32}S, between the released sulfur and background or natural sources, can be utilized to identify the source of the material found on the receptor (Krouse et al. 1977) thereby allowing computation of deposition arising from a particular source. Release of additional tracer is not always necessary if an existing source, such as a sour gas well, has an isotopic ratio sufficiently different from other background sources.

A different type of approach, namely a dual tracer study, has been described by Sehmel (1983). It involves the controlled release of two tracers, one whose deposition is of interest and another which is known to be non-depositing. Concentrations of both tracers are monitored in the plume downwind of the release, and deposition is deduced from the changes in the concentration ratio of deposited to non-deposited tracer with increasing downwind distance from the release point. The method is particularly suited to computation of dry deposition losses from plumes and may provide insights on deposition processes that are applicable to larger-scale deposition problems.

Cuvettes and Chambers

Leaf cuvettes or controlled environment chambers have been used to measure deposition rates, particularly for gaseous pollutants. They are particularly useful for defining mechanisms because of their large degree of environmental control. However, because they alter the environment, they do not necessarily reproduce deposition under natural conditions, and the representativeness of results obtained from them must be carefully considered. Deposition or emission is determined by evaluating mass balance for the species of concern. In dynamic systems deposition or emission is equated to differences in mass inflow and outflow from the system, after correcting for losses or gains associated with the chamber walls. In static systems emission or deposition is deduced from changes in concentration over time after the system is sealed. Corrections for changes in atmospheric concentrations of other gases, particularly water vapor, may be necessary (Leuning 1983).

Mass Budgets

Mass budgets or balances may also be applied on larger scales to deduce mean deposition (or emission) rates. In carefully calibrated drainage basins or watersheds it may be possible to define quantitatively all sources and sinks of a particular element, for example sulfur, except for the atmospheric dry input. Measuring temporal changes in these various reservoirs will allow dry deposition to be estimated as the material needed to balance the various changes in the system over the time interval. Although simple in principle, the method is difficult to apply in practice because the precision needed in specifying the content in the various reservoirs in order to discriminate a relatively small dry deposition is not often attainable. In other cases, not all other sinks and sources can be quantified, for example groundwater loss from the basin. Mass balances can also be attempted on atmospheric scales by computing atmospheric inflows and outflows across geographically closed boundaries. If internal sources or chemical transformations can be accounted for, the net loss of material over time scales in the order of several days or weeks can give a measure of deposition. The experimental demands of such measurements are very severe and they are rarely attempted.

Computation from Ambient Concentrations

Deposition can be calculated from measurements of ambient concentrations provided that the resistances to deposition can be defined for the area of interest. The use of a constant deposition velocity multiplied by concentration to give deposition rate is the simplest application of this approach, but this simple method is a poor analogue of the physical process and is of doubtful validity except over long averaging periods. The resistance analogue outlined earlier provides a framework for applying micrometeorological knowledge on the relationship of fluxes to mean atmospheric and surface properties to the problem of dry deposition (Shieh et al. 1979). In principle it should provide a much more realistic depiction of deposition than a constant V_d on scales as short as 1 hour. It is at present the only practical method of routinely estimating deposition on spatial scales of tens of kilometers. Surface properties may be estimated from land-use maps showing extent and type of surface cover, and allowance made for known seasonal variations in surface properties. Representative meteorological and concentration data are also required, and it is somewhat problematical whether available networks have been completely adequate in spatial density and representative siting. The concentration-resistance analogue approach is being actively pursued at the Atmospheric Environment Service (AES) to application of Long Range Transport of Air Pollution (LRTAP). Early results from this program showing typical outputs are shown in Figure 11 (Masse and Voldner 1981). This particular output has been derived using climatological information for the month of April and gives isolines of computed deposition velocities. The snow-cover line is included since deposition velocities can change markedly when terrain becomes snow-covered. The 10°C isotherm has been used as a measure of vegetative growth. Figure 11 is included for illustrative purposes. It represents an interim output subject to revision after evaluations of the parameterization schemes are completed.

AMBIENT CONCENTRATIONS IN EASTERN NORTH AMERICA

Ambient concentrations of various air pollutants have been measured by national networks over a number of years in both Canada (National Air Pollution Surveillance Network) and the United States (National Air Surveillance Network, Inhalable Particle Network). These networks were designed primarily to protect human health and accordingly monitoring stations were primarily located in population centers. They can provide only limited information on pollutant concentration in forested areas. In some instances these national networks have been augmented, for example local networks about potential point-source polluters, such as ore smelters, or regional networks such as the Air Monitoring Network (Ontario Ministry of the Environment) in southern Ontario. Nevertheless, measurements in forest environments are relatively rare.

The measurements from urban networks are largely influenced by local sources of pollution and are not overly useful in quantitatively assessing the impact of long-range transport of air pollution (LRTAP).

After long range transport and acid deposition were recognized as serious problems in eastern Canada, it was also realized that existing air monitoring stations did not fulfill the needs for reliable measurements of regional-scale air quality on a national scale. Consequently in 1978, the Atmospheric Environment Service established the Air Pollution Network (APN) with sampling and siting protocols designed to provide regionally representative, non-urban monitoring. This network has recently been reorganized as the Canadian Air Pollution Monitoring Network (CAPMoN). Figure 12 shows the distribution of the network monitoring sites as of 1982. The stations have been situated from Saskatchewan eastward in the area perceived to be most likely subject to LRTAP and acid precipitation. At each station integrated daily samples of sulfur dioxide and airborne particulates are collected on separate, but in-line, filter packs. The daily samples are sent to a central laboratory for analysis. Particulate samples are analysed for sulfate, total nitrate, chlorine, sodium and ammonium ions. Samples from Long Point have also been analysed for bromine, vanadium, aluminum, manganese and calcium. Air concentrations are computed from measured filter deposits and the measured, total amount of air flowing through each filter over the sample period. A similar nationally operated network for routine data collection has not yet been established in the United States. Specialized networks of limited duration have been operated periodically, for example, for the Sulfate Regional Experiment (SURE) in 1978 (Figure 13) sponsored by the Electric Power Research Institute (EPRI).

Data from the APN network have provided some insight on the nature of air pollution away from local sources. Air pollution has been found to be highly episodic, as illustrated in Figure 14 (from Barrie et al. 1980) for sulfur dioxide (SO_2) and airborne sulfate (SO_4^{2-}) measured at ELA Kenora over the period November 1978 to June 1979. Episodes typically last several days and are interspersed with periods of essentially clean air. Consistent seasonal patterns are also evident in the data which depend somewhat on station location. Mean monthly SO_2 and SO_4^{2-} concentrations over the year 1979 are shown in Figure 15 (from Barrie 1982) for the stations at Long Point, Chalk River, Kejimkujik and ELA Kenora. SO_2 shows a strong winter maximum at all stations but SO_4^{2-} shows a summer maximum, except at ELA Kenora. This seasonal variation is believed to reflect temperature-dependent changes in the SO_2-SO_4^{2-} conversion rate in the atmosphere and in the scavenging efficiency rather than seasonal changes in emission rates. Figure 15 also indicates that concentrations decrease with increasing distance from the Lower Great Lakes. This is further shown by the mean annual concentrations for 1981 given in Table 2 (derived from Barrie et al. 1982). This association of higher concentration with proximity to the Lower Great Lakes is most likely associated with relative distance from major emitters of sulfur to the atmosphere. Figure 16 gives annual SO_2 emissions considered representative of 1980 as incorporated in the Canada-United States Memorandum of Intent on Transboundary Air Pollution (1982). Broadly speaking, the major source region is centered along the Ohio River valley just south of Lake Erie. There is good correlation between air parcel back-trajectories and SO_4^{2-} air concentrations. Figure 17 (from Anlauf et al. 1980) shows computed 4-day back-trajectories from Toronto, Ontario, for 3 days in 1976: August 16, a day with low SO_4^{2-}, and August 21 and 22, days with high SO_4^{2-}. Trajectories along constant pressure surfaces of 85 kPa and 100 kPa are given, corresponding approximately to 1500-m and surface altitudes respectively. Low-pollution days, typified by August 16, are invariably associated with air trajectories over low-emission northerly sectors. High-pollution days are associated with trajectories passing over high-emission regions to the south and southwest of Toronto as on August 22, or stagnating episodes such as August 21 which, for Toronto, allow build-up of SO_4^{2-} due to the appreciable local emissions (see Figure 16). The episodic behavior in pollutant concentration noted earlier is associated with changing air mass trajectories to the monitoring sites rather than local variations in sources.

Spatial patterns of atmospheric concentrations of SO_2, SO_4^{2-} and other atmospheric pollutants can be generated from numerical LRTAP models. These patterns can then be used to supplement data from the sparse monitoring networks, taking account, however, of the fact that the simplification of the complex atmospheric processes of transport and chemistry by the models introduces a degree of uncertainty into their results. An example of model-generated concentration and deposition fields is given by Olson et al. (1982). They employed a 4-day back-trajectory computation (Olson et al. 1978) at 6 h timesteps to derive the path of air parcels reaching designated receptor points in eastern Canada at 6 h intervals for each day over an annual period using archived wind fields for 1978. Concentrations of pollutants within these air parcels were computed over the trajectories by a simple box model beginning 4 days before arrival at the designated receptor and advancing in 3 h time-steps. This computation was achieved by following the air parcel trajectory across a fixed rectangular grid over eastern North America, which defined the box pattern for computation. The concentration of the arriving air parcel following a time step defined the initial concentration within the relevant box. This concentration was then adjusted for the effects over one time step of inputs for the particular box based on the available emissions inventory, dry deposition using constant deposition velocities (1.0 cm s^{-1} for SO_2, 0.1 cm s^{-1} for SO_4^{2-}), linear conversion of SO_2 to SO_4^{2-}, and, if precipitation was observed, washout based on a constant scavenging ratio. The concentration computation assumed complete mixing within each box throughout the height of the surface mixed layer, the latter being the monthly climatological average value. This new concentration was assigned to the air parcel at the end of the next time step after the parcel was moved along the trajectory to the next appropriate box. This computational process was repeated until the parcel reached its designated receptor point. These end-point concentrations, computed four times a day, were then averaged over the year at each receptor point to give the annual concentration fields for SO_2 (Figure 18) and SO_4^{2-} (Figure 19). These patterns reproduce the observed reduction in concentration in eastern Canada with distance from the Lower Great Lakes, but for SO_2 also show a second maximum near the southwest corner of Quebec due to emissions from the major point source at Sudbury, Ontario. The model also generates deposition fields based on computed washout for wet deposition (Figure 20) and the concentration fields multiplied by the assumed deposition velocities for dry deposition (Figure 21). Computed dry deposition of sulfur ranged from 30 to 60 kg ha^{-1} over southern Ontario dropping off to less than 1 kg ha^{-1} over northern regions. Computed wet depositions of sulfur were only one-third to one-half dry deposition over southern Ontario, but declined less rapidly away from source regions than dry deposition so that computed input from wet and dry were comparable in the northern segment. These general patterns in wet and dry deposition are consistent with observations, but actual magnitudes and wet/dry ratios may depart somewhat from the modeled results. There is some evidence that the modeled results in this example yielded over-estimates of pollutant concentrations due to an over-estimate of source strengths in the emission inventory (Olson 1983 — personal communication).

Observations suggest that SO_2 and SO_4^{2-} concentrations in eastern North America are comparable to those in western Europe. Mean annual APN data for 1981 are given in Table 2, and observed mean annual concentration fields over Europe (derived from preliminary data EMEP) for the same year are shown in Figure 22 for SO_2 and in Figure 23 for SO_4^{2-}. Concentrations in heavily industrialized areas of Europe were similar to those reported at Long Point and Chalk River in Ontario, the latter presumed to be influenced by emissions from Sudbury for this particular year, while concentrations in relatively pristine areas of eastern Canada typified by ELA Kenora were similar to the least polluted measurements in Europe along its Atlantic fringe. In terms of dry deposition of sulfur, therefore, western Europe and eastern Canada appear to face similar problems.

Table 2. Mean annual concentration for 1981
APN data

	SO_2 µg m^{-3}	SO_4^{2-} µg m^{-3}
Long Point	16.5	4.9
Chalk River	8.5	1.5
Algoma	3.6	2.4
Montmorency Forest	2.7	2.0
Kejimkujik	1.7	1.8
ELA - Kenora	1.0	1.2

MEASURED DRY DEPOSITION VELOCITIES

Direct measurements of dry deposition in the field are rare as experimentally determined values usually assume deposition from some other measurements. Radioactive tracers provide perhaps the most direct measurement of deposition, but are best suited for controlled environment studies for technical and safety-related reasons. Micrometeorological studies adopt deposition from measured atmospheric eddy fluxes above the surface. This may give improper deposition values in certain circumstances, but in general the micrometeorological methods are considered to give reliable estimates of deposition in properly conducted experiments. The budgeting techniques may also provide good estimates of deposition over large areas for relatively long averaging periods. However, the methods are less direct than micrometeorological measurements, and sources of error are often more difficult to quantify or sometimes even identify. Results from artificial collectors are most difficult to relate to actual deposition. Gaseous deposition to natural surfaces, particularly vegetative surfaces, is very poorly reproduced by even carefully designed surrogates unless the gas is quite reactive to all exposed surfaces. The situation for particle collection is little, if at all, better since deposition depends so much on both macro-structure of the collector and the micro-structure of its surface. Hence measurements from artificial collectors are considered least reliable.

Recent deposition measurements are summarized by Hicks (1983). For vegetative surfaces not under severe water stress, daytime deposition velocities for SO_2 have ranged from 0.4 cm s^{-1} to near 2.0 cm s^{-1}, with a median value near 1 cm s^{-1}. Values of 0.1 to 0.2 cm s^{-1} have been found at night, or for water-stressed vegetation with closed stomata. Similarly, low V_d has been found for non-reactive surfaces such as dry snow whereas much higher rates have been noted for wet surfaces. Deposition velocities to vegetative surfaces, typically 0.5 to 1.5 cm s^{-1}, have been found for ozone and NO_2, and daytime values in this range may be considered typical for gases primarily absorbed via stomata. Reactive gases such as HNO_3 (Huebert 1983) can be expected to have deposition determined by atmospheric transport only, and for short vegetation deposition velocities typically lie in the range 2 to 5 cm s^{-1}.

The physical processes involved in the deposition of atmospheric particles are not as well known as those for most gases. Stomatal opening is unlikely to influence deposition significantly, but particle size can be expected to play a dominant role. This dependence should be kept in mind when reviewing results on particle deposition. Particle deposition is also summarized by Hicks (1983). For particles $\leq 0.1\ \mu m$ in diameter, estimated deposition velocities from micrometeorological studies over vegetated surfaces have ranged from near 0.1 cm s^{-1} (Garland and Cox 1982) up to near 1.0 cm s^{-1} (Hicks et al. 1982) for periods of a few hours during the afternoon. Deposition of these very fine particles is complicated by apparent small upward fluxes at night and early morning which may reflect surface gaseous emissions and subsequent gas-to-particle conversions, or they may be experimental artifacts due to humidity-particle size interactions (Wesley et al. 1983a). As yet, few measurements of deposition of particles in the size range 0.1 to a few microns, corresponding to the typical atmospheric maximum in the accumulation region, have been made. The available measurements (Sievering 1982, 1983; Katen and Hubbe 1983; Neumann et al. 1983; Wesley et al. 1983b) seem to suggest small deposition rates for such particles ($V_d < 0.1$ cm s^{-1}). Large-particle deposition (diameters $> 10\ \mu m$) is not amenable to micrometeorological flux determination, but neither is it considered of importance in LRTAP, although it may represent the dominant transfer due to local sources. Some measurements have also been made of sulfate deposition to a pine forest by using a total-sulfur analyser when no gaseous sulfur was detected (Hicks et al. 1982). Deposition velocities averaging near 0.7 cm s^{-1} have been measured, which are comparable to gaseous deposition rates. However, for these particular experiments the size distribution of sulfate particles was not determined and there is some possibility of water vapor interference in the sulfur measurement (Tanner et al. 1980).

SUMMARY

Dry deposition is a complex process involving chemical, biological and meteorological factors. Deposition may result from adsorption of gaseous components, such as SO_2 and NO_2, or from entrapment of atmospheric particles. The atmospheric particles of most concern in terms of acidic deposition and long-range transport are sub-micron particles containing sulfates and nitrates. They arise from chemical transformations of gaseous precursors within the atmosphere. The mechanisms for deposition of these very fine particles are more complicated and less well quantified than those for gaseous deposition. Sedimentation is thought to play only a minor, and perhaps insignificant, role. Dryfall collectors such as buckets or flat plates are inadequate to quantitatively measure sub-micron particle deposition to natural surfaces and they neglect gaseous phase deposition. Suitably exposed surrogate surfaces or periodic sampling of natural receptors have been used to obtain spot estimates of deposition to natural surfaces, but problems of calibration and extension of point-measurements to give canopy deposition rates are not yet totally resolved. In principle, micrometeorological methods can provide good estimates of deposition rates to vegetative canopies and other natural surfaces but have stringent requirements for site suitability and instrumentation. They are more suitable for intensive studies aimed at parameterization of the transport mechanisms rather than for routine monitoring of deposition. For longer-term estimation of dry deposition input on regional scales, the most practical approach appears to be to delineat the atmospheric concentration fields of the relevant pollutants and then to utilize appropriate parameterization schemes for deposition rates which incorporate meteorological and surface factors in a realistic manner.

The current networks of non-urban air monitoring stations in eastern North America are sparse. However, the Canadian APN (recently revised to CAPMoN) monitoring stations have provided insights on regional distributions of SO_2 and particulate pollution in eastern Canada. Concentrations decline with distance from major source regions, but impacts are still evident hundreds of kilometers downwind of source regions. Pollution events are episodic in nature, and can be related to the trajectory of arriving air-parcels relative to emission sources. Diurnal variations arising mainly from changes in turbulent transport near the surface as a function of atmospheric stability are superimposed on the episodes. The variability in atmospheric concentration, hence dry deposition, is such that several years of data are usually required to define a stable or consistent mean value. Even longer periods are required to indicate trends reliably. Absolute SO_2 and sulfate pollution levels in eastern Canada are comparable to western Europe, with mean concentrations along the Lower Great Lakes similar to those near industrial complexes in central western Europe while concentrations in forested regions of northern Ontario and Quebec appear similar to those found in Scandinavia.

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DISCUSSION

Question: What is the relationship between changes in elevation and rates of dry deposition inputs?

Answer: One would expect there to be some relationship in terms of the effect of elevation on the meteorology or the exposure and that you would have more efficient rates of transfer from the atmosphere at higher elevations. There are no actual measurements that have looked at the problem.

Question: Most ecologists believe that forests are better than low vegetation at capturing sulfur from SO_2 and from particulate SO_4 but deposition velocities to forests are usually quoted as being slightly lower than for grasses. Is this a contradiction? Which do you believe?

Answer: Gaseous deposition of sulfur dioxide to a forest is a form of dry deposition. For canopies that are unwetted by rain, fog or dew, the primary mode of uptake is via the stomates. In general the stomatal resistances of forests are larger than those of grasses and other low vegetation on a per unit leaf area basis in the absence of water stress. The greater stomatal resistances tend to compensate for the better exposure of forests to atmospheric turbulence so that net transfer rates to forests and to low vegetation are similar. This is reflected by similar net evaporative water losses from forests and grasslands when soil moisture is non-limiting. Thus the rates of deposition of gases such as sulfur dioxide which normally do not react with exterior cuticular surfaces do not vary substantially between forests and grasslands. However, for a gas that is absorbed or reacts at the exterior vegetative surfaces, the greater exposure of canopy elements in a forest would result in appreciably larger deposition velocities to forests than to grassland. This situation would arise for sulfur dioxide deposition to wet canopies.

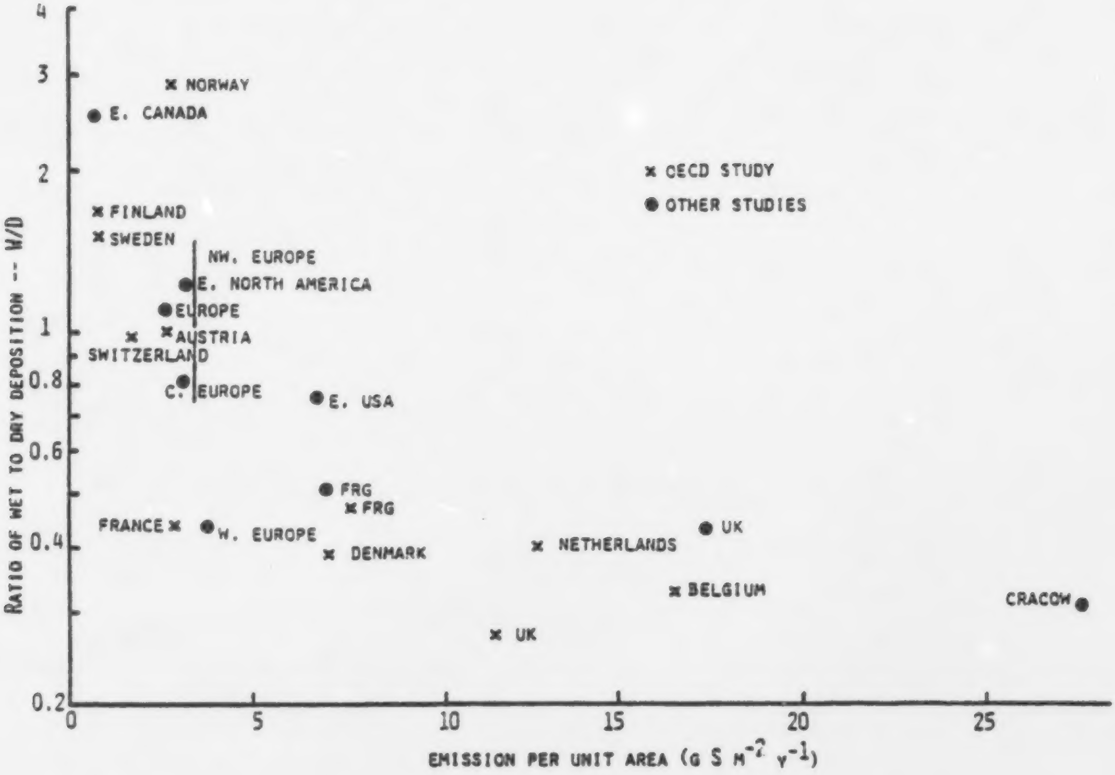
Data on particle deposition to natural surfaces are very limited and little work has been done on particle deposition to forests in particular. More is known on particle deposition to grasses mainly as a result of measurements made in wind tunnels. However, since particle deposition is probably non-stomatal, one can speculate that the greater exposure of forests to wind and turbulence would result in relatively larger deposition rates to forests than to grasslands. Because data on measured deposition rates for both gases and particles to forests are very sparse, our group at the Atmospheric Environment Service will shortly be initiating a forest dry deposition study.

Question: Does cloud-seeding for inducing rain affect acid-rain deposition?

Answer: If cloud-seeding were effective, yes, the rate would increase locally where extra precipitation occurred, but this would be at the expense of deposition further downwind.

Question: Why is the H^+ concentration higher in summer and lower in winter? Is this due to greater emissions in summer or atmospheric processes?

Answer: A combination of both.



$g\ S\ m^{-2}\ yr^{-1}$

Figure 1. Relative importance of wet and dry deposition as a function of emission density (Whelpdale and Galloway 1979).

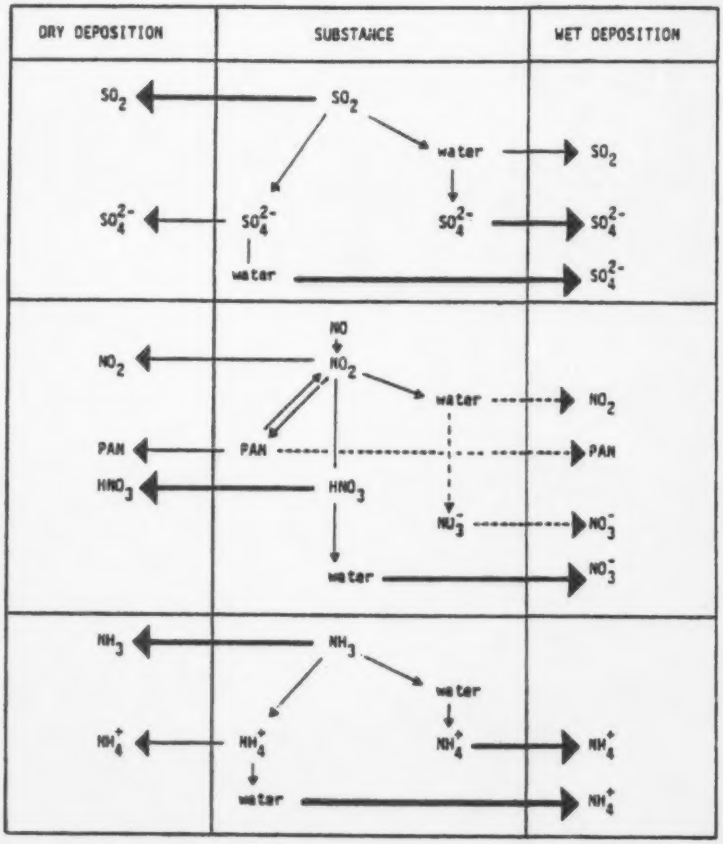

DRY DEPOSITION
SUBSTANCE
WET DEPOSITION
SO_2
SO_2
water
SO_2
SO_4^{2-}
SO_4^{2-}
SO_4^{2-}
SO_4^{2-}
water
SO_4^{2-}
NO
NO_2
NO_2
water
NO_2
PAN
PAN
PAN
HNO_3
HNO_3
NO_3^-
NO_3^-
water
NO_3^-
NH_3
NH_3
water
NH_4^+
NH_4^+
NH_4^+
NH_4^+
water
NH_4^+

Figure 2. Schematic diagram of possible deposition pathways for the major acidic species. The middle column depicts processes or steps along the pathway prior to deposition. The horizontal arrows depict deposition processes for the various species: to the left indicates dry deposition; to the right indicates wet deposition. Heavy lines represent important pathways and broken lines represent uncertain ones (Ferguson & Machta-MOI Report 2F, 1982).

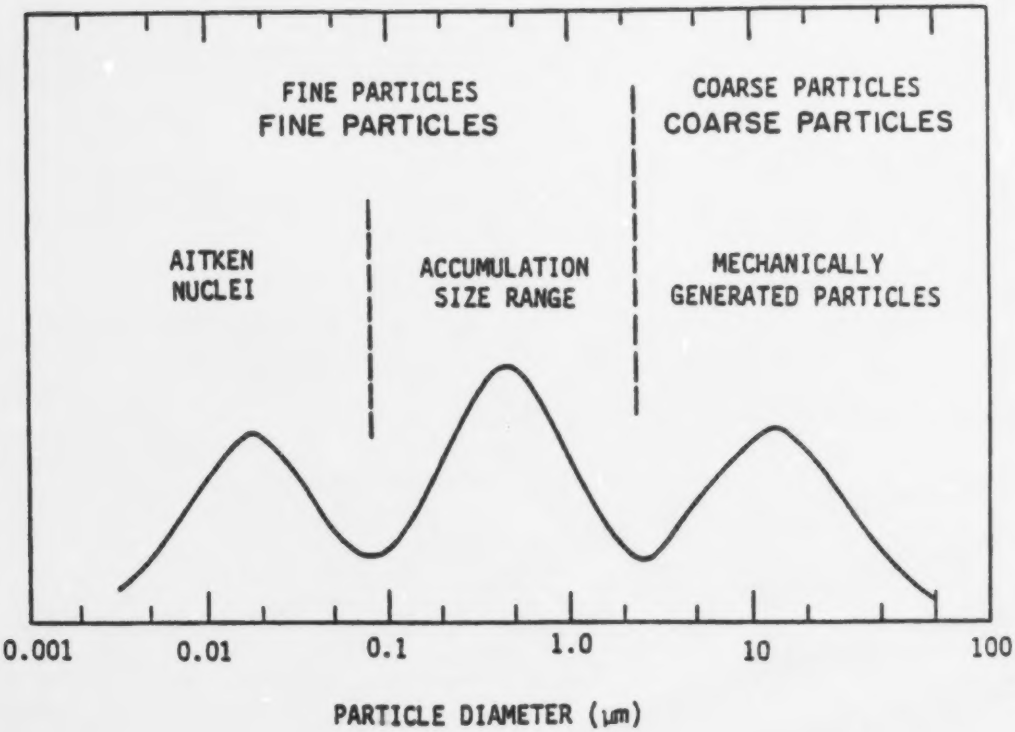


Figure 3. A hypothetical particle size spectrum, as might be found downwind of an industrial complex (Hicks 1983).

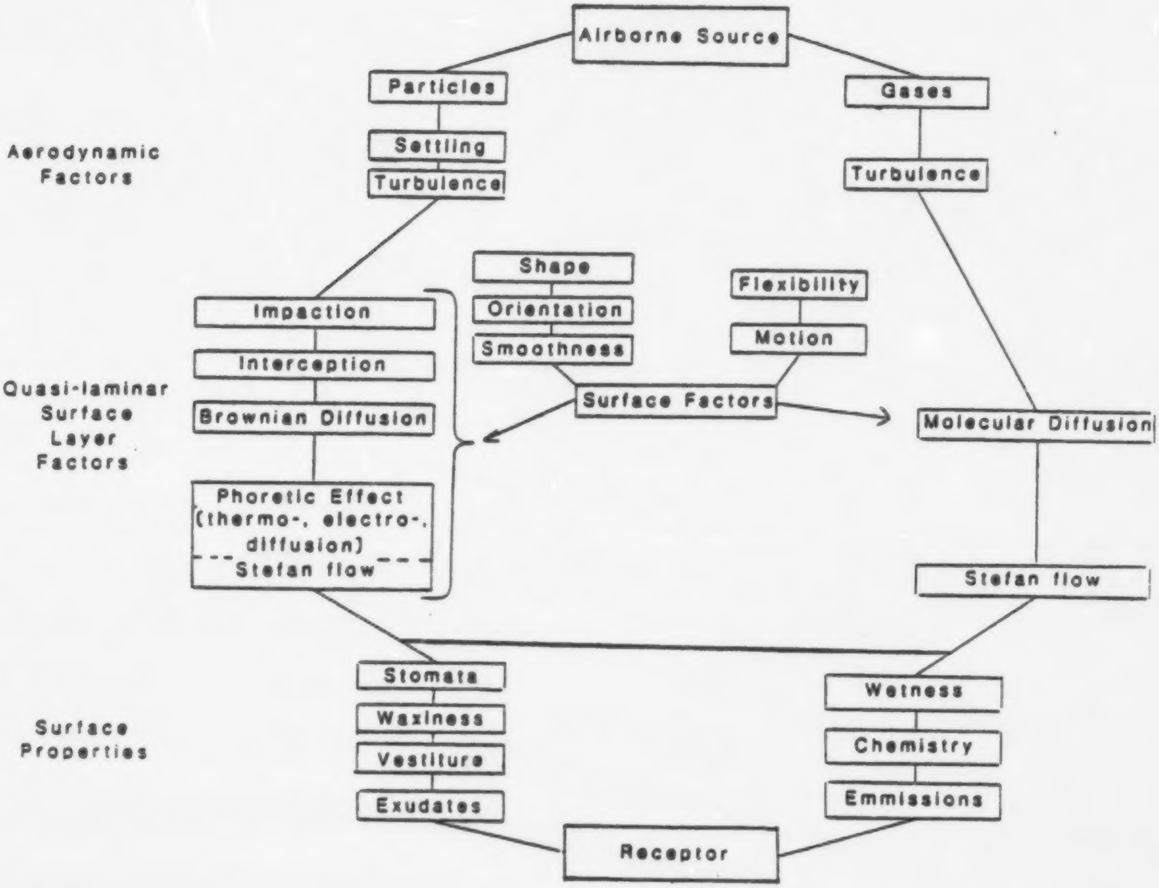

Airborne Source
Particles
Gases
Aerodynamic Factors
Settling
Turbulence
Turbulence
Shape
Orientation
Smoothness
Flexibility
Motion
Surface Factors
Quasi-laminar Surface Layer Factors
Impaction
Interception
Brownian Diffusion
Phoretic Effect (thermo-, electro-, diffusion)
Stefan flow
Molecular Diffusion
Stefan flow
Surface Properties
Stomata
Waxiness
Vestiture
Exudates
Wetness
Chemistry
Emmissions
Receptor

Figure 4. A schematic representation of processes or factors likely to affect dry deposition. Processes for particles and gases are likely to be different but many factors influencing these processes are shared. The effect of processes shown for particle deposition will vary with particle size (after Hicks 1983).

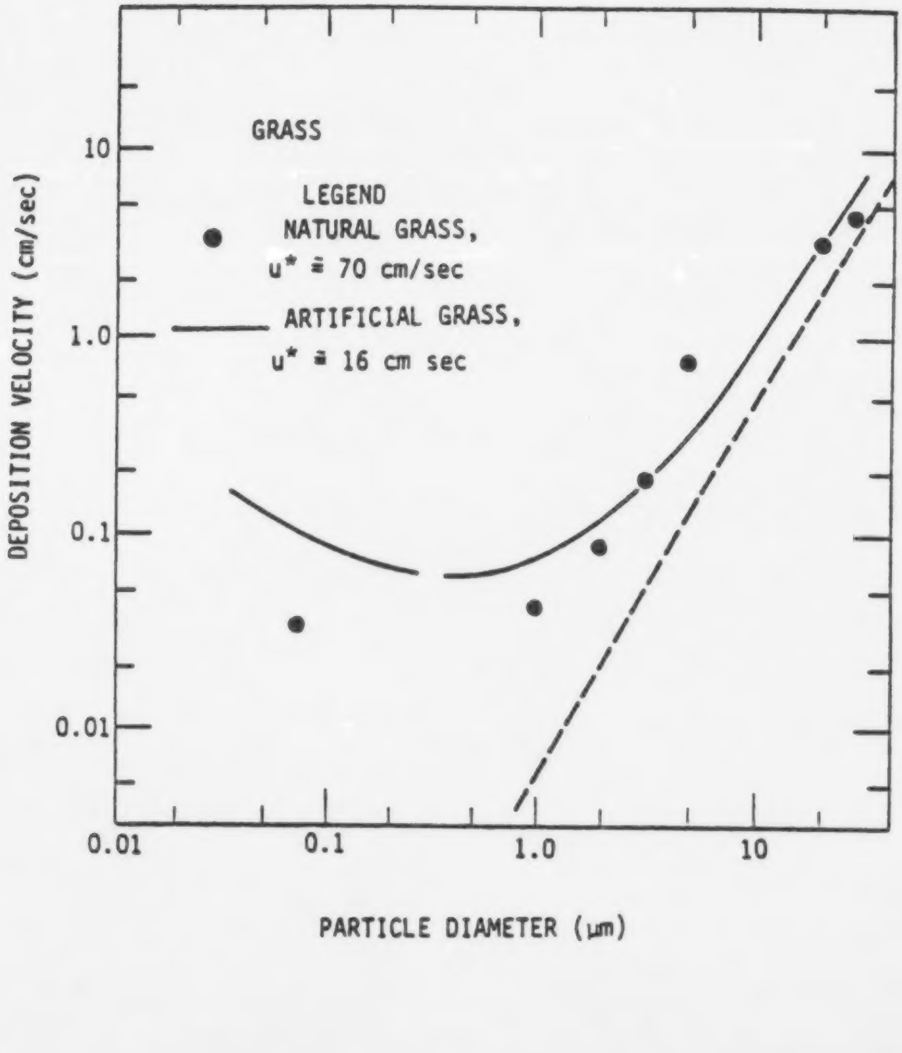
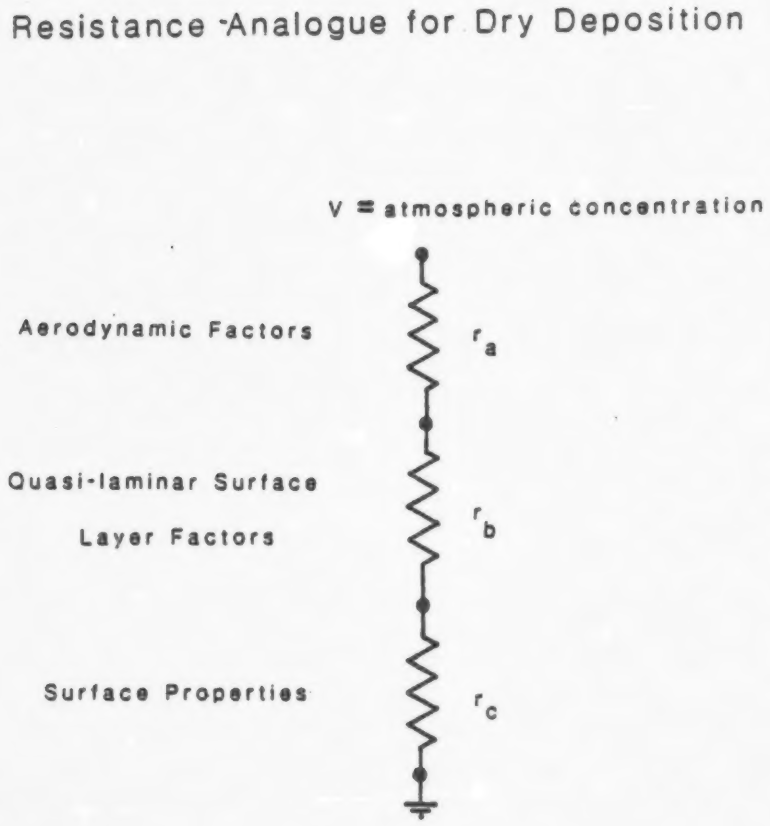


Figure 5. Results of wind tunnel studies or particle deposition to grass as given in the review by Hicks (1983). The dotted line represents computed deposition rate due to gravitational settling.


Resistance Analogue for Dry Deposition
V = atmospheric concentration
Aerodynamic Factors
r_a
Quasi-laminar Surface
Layer Factors
r_b
Surface Properties
r_c

$$\text{Rate of Deposition} = \frac{V}{r_a + r_b + r_c}$$

Figure 6. A simple resistance model or the dry deposition pathway from the atmosphere to terrestrial surface. The aerodynamic term, r_a, is controlled by turbulence and is strongly influenced by stability. The r_b term is determined by the elementary properties of the deposited material - molecular diffusivity for gases, or for particles, impaction, interception and Brownian diffusivity. It is strongly affected by surface roughness. The r_c term represents the residual resistance necessary to quantify the overall deposition and includes the specific effects of surface properties such as stomatal opening and chemical reactivity.

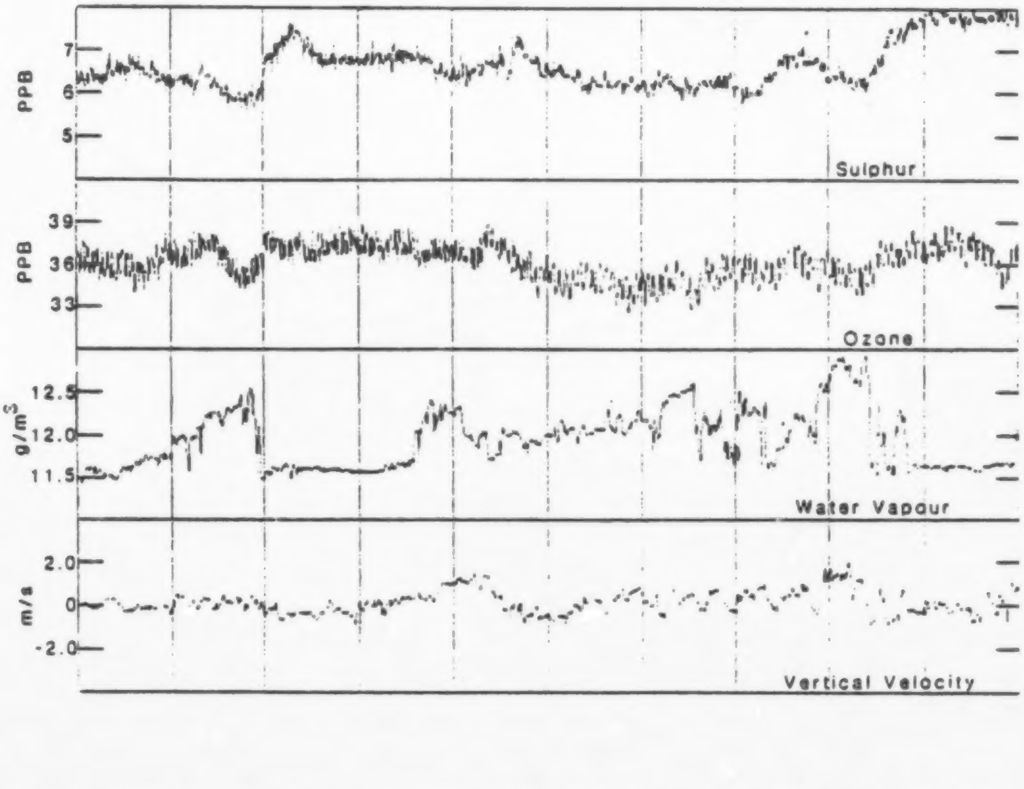


Figure 7. Measured atmospheric parameters at 4.5 m for 12:06 to 12:07 pm CDT, June 25, 1982, during the dry deposition intercomparison study at Champaign, Ill.

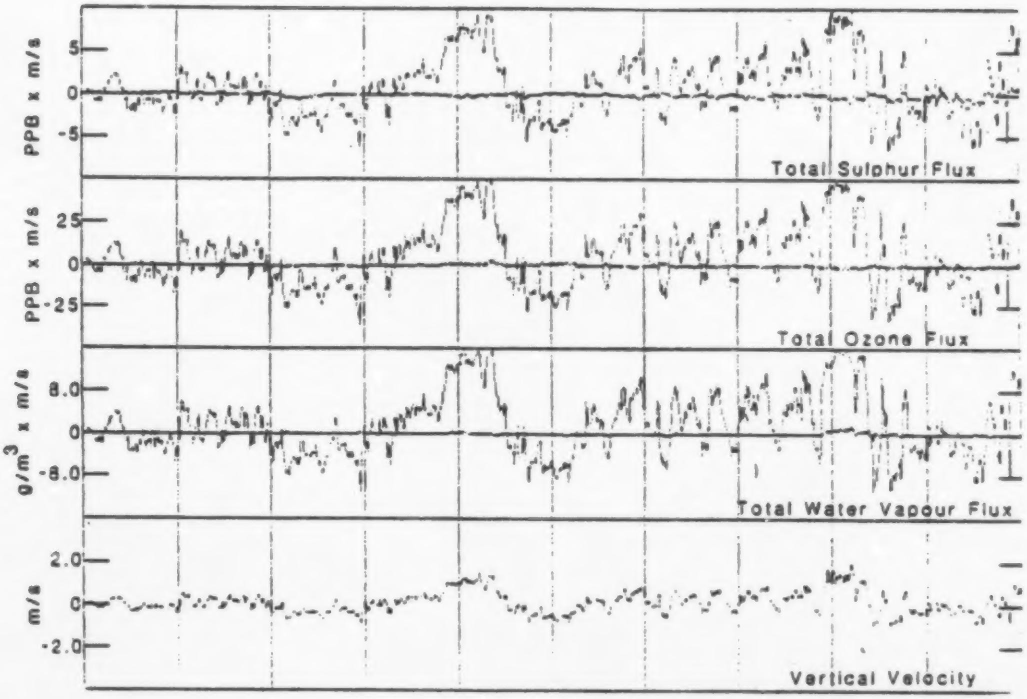


Figure 8. Atmospheric fluxes and vertical velocity at 4.5 m for 12:06 to 12:07 pm CDT, June 25, 1982, during the dry deposition intercomparison study at Champaign, Ill. Both total and eddy fluxes are shown.

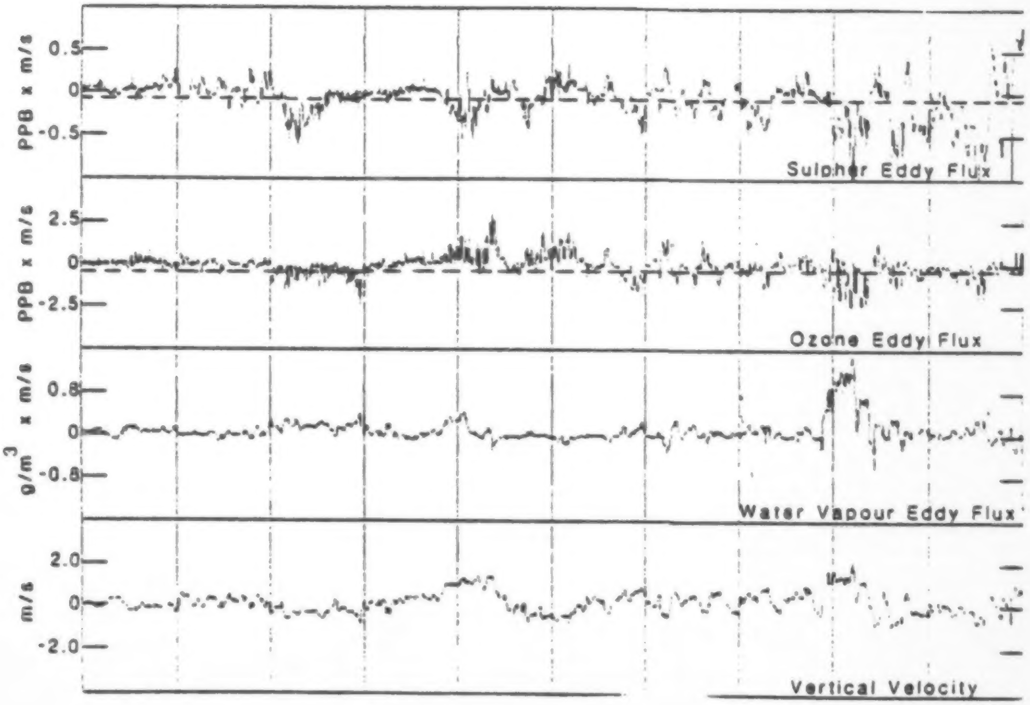


Figure 9. Atmospheric eddy fluxes and vertical velocity at 4.5 m for 12:06 to 12:07 pm CDT, June 25, 1982, during the dry deposition intercomparison study at Champaign, Ill. For reference equivalent constant flux for $V_d = 1.0 \text{ cm s}^{-1}$ are shown by dashed lines.

Resistance Analogy for Plant-Soil System

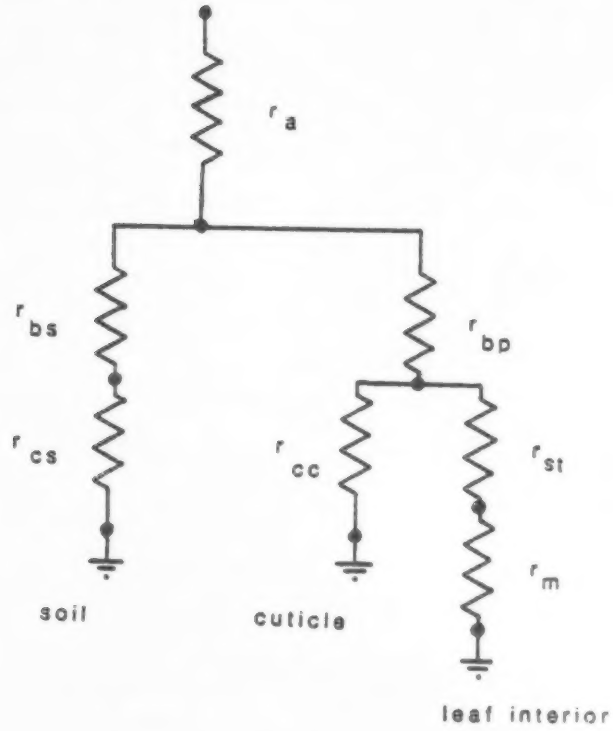


Figure 10. A more elaborate, yet still highly simplified, resistance model for deposition showing separate pathways for deposition to the soil and to a plant canopy. For the plant separate sinks are shown for the cuticular surface and the interior leaf surface as would be appropriate for gaseous uptake. Transfer to the leaf interior is regulated by the stomatal resistance, r_{st}, and a residual "mesophyll" resistance, r_m, has been found to be near zero for O_3 and SO_2 transfer, but not always for CO_2 transfer.

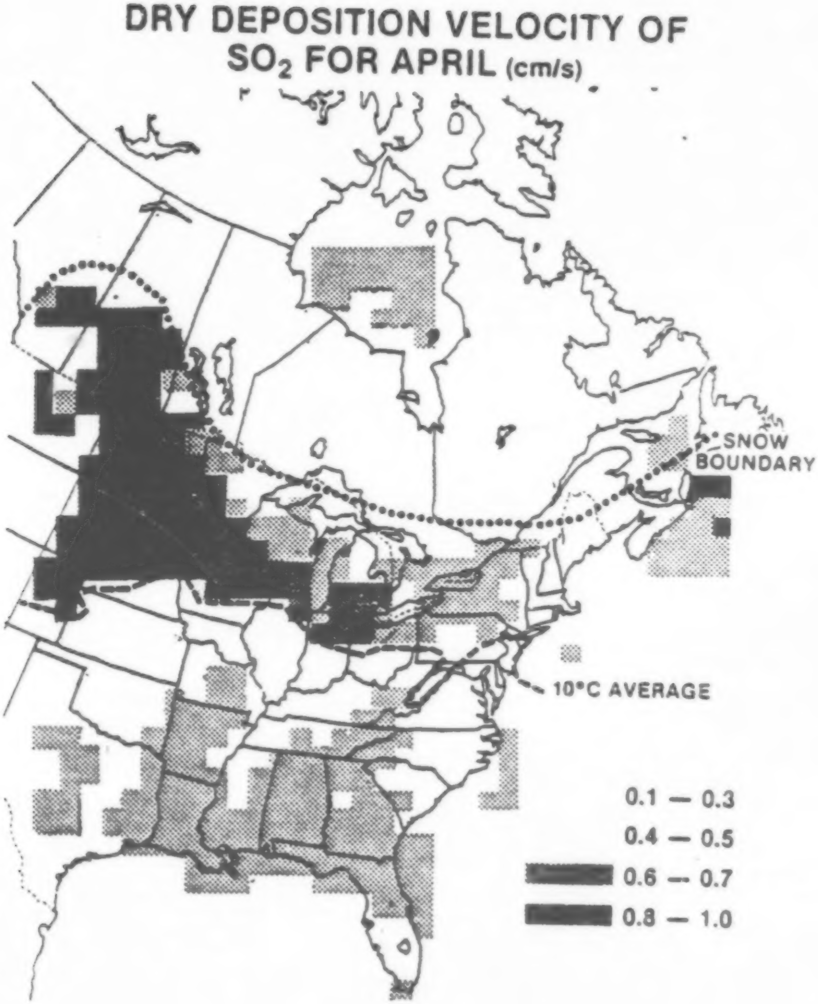

DRY DEPOSITION VELOCITY OF
SO₂ FOR APRIL (cm/s)
SNOW BOUNDARY
10°C AVERAGE
0.1 — 0.3
0.4 — 0.5
0.6 — 0.7
0.8 — 1.0

Figure 11. Computed dry deposition velocity field for SO_2 based on climatological mean weather parameters for April and on gridded land-use categories (Masse and Voldner 1983).

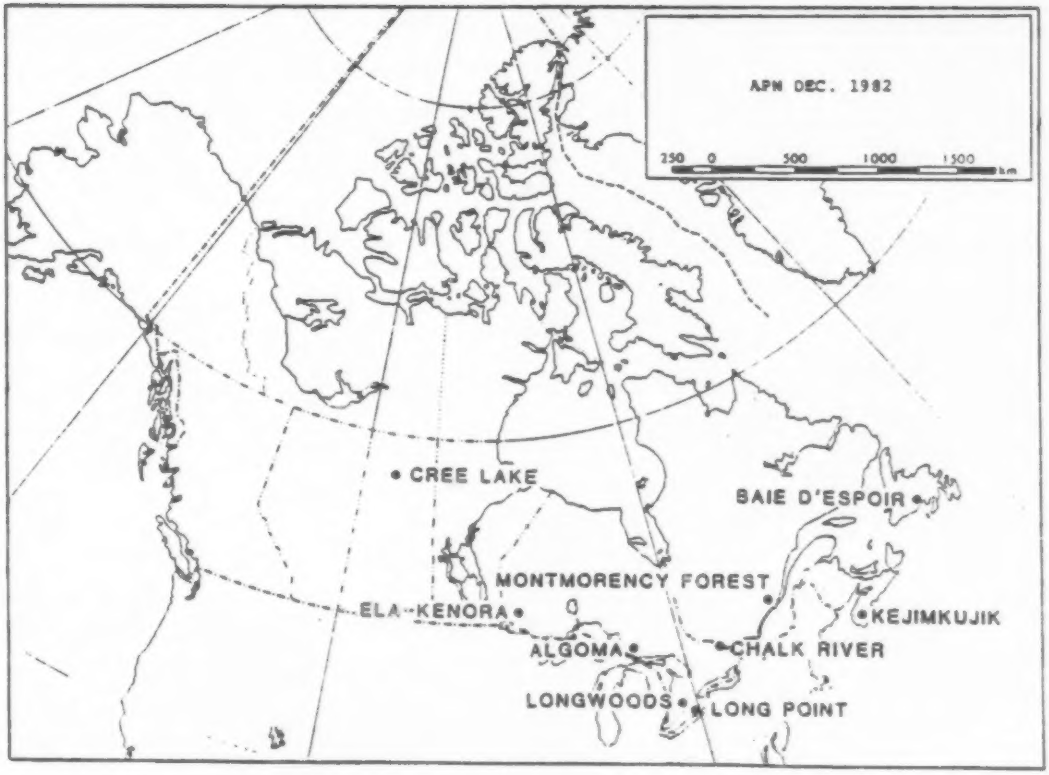

APN DEC. 1982
250
0
500
1000
1500
km
CREE LAKE
BAIE D'ESPOIR
MONTMORENCY FOREST
ELA-KENORA
KEJIMKUJIK
ALGOMA
CHALK RIVER
LONGWOODS
LONG POINT

Figure 12. Stations in the Canadian APN network (Barrie et al. 1982).

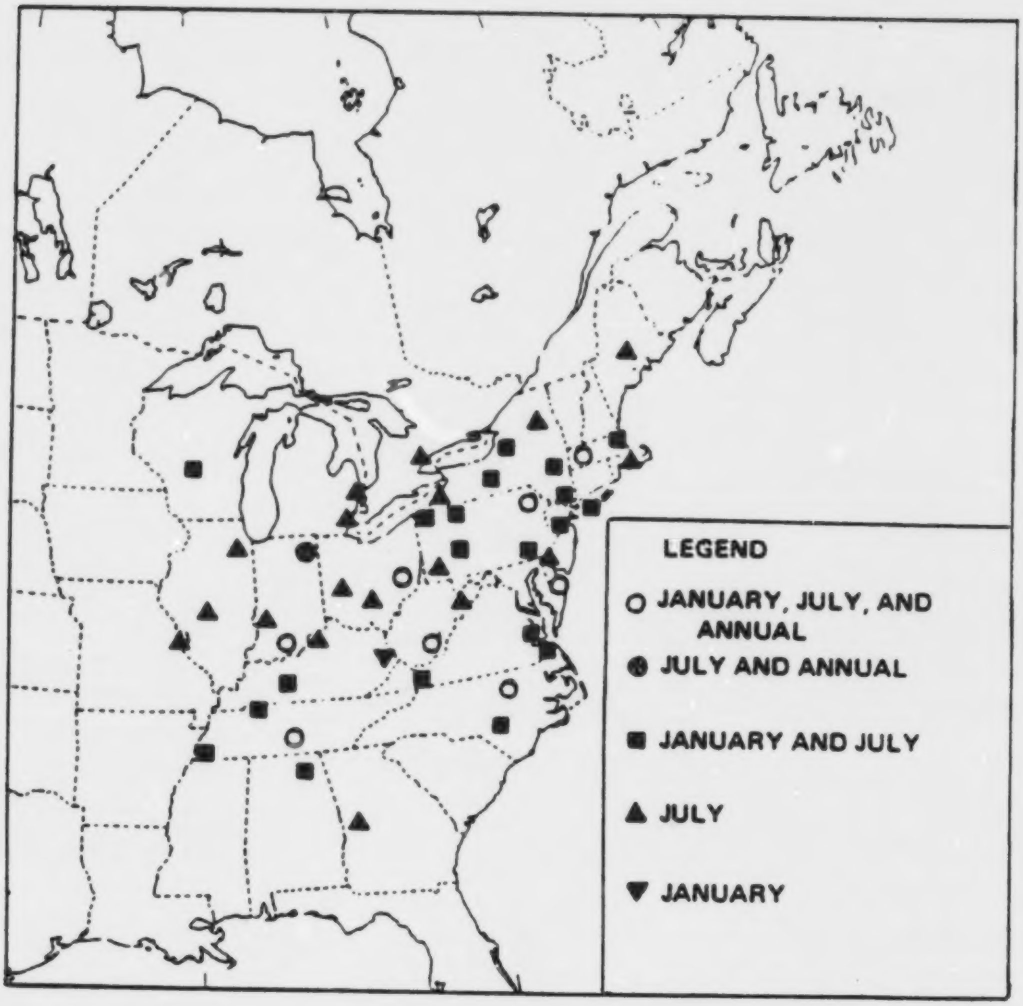

LEGEND
○ JANUARY, JULY, AND ANNUAL
⊗ JULY AND ANNUAL
■ JANUARY AND JULY
▲ JULY
▼ JANUARY

Figure 13. Stations in the EPRI SURE study during 1978. The legend indicates acceptable data capture for January, July and annual verification periods in the MOI document. During the SURE study Class I and Class II were operated, the former continuously and provided annual data for this figure, but the latter were operated only during intensive periods (January 10 to February 10, April, July and October, 1978) (MOI Report 2F-M).

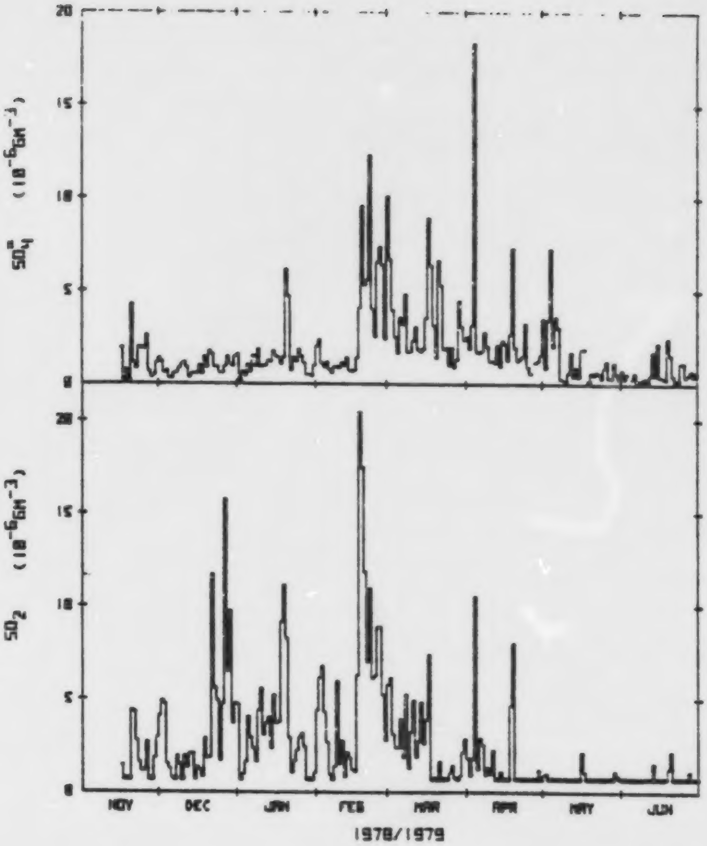


Figure 14. Daily sulfate and SO_2 concentrations in the air measured at the Experimental Lakes (ELA-Kenora) APN station for the period November 1978 to June 1979 (Whelpdale and Barrie 1982).

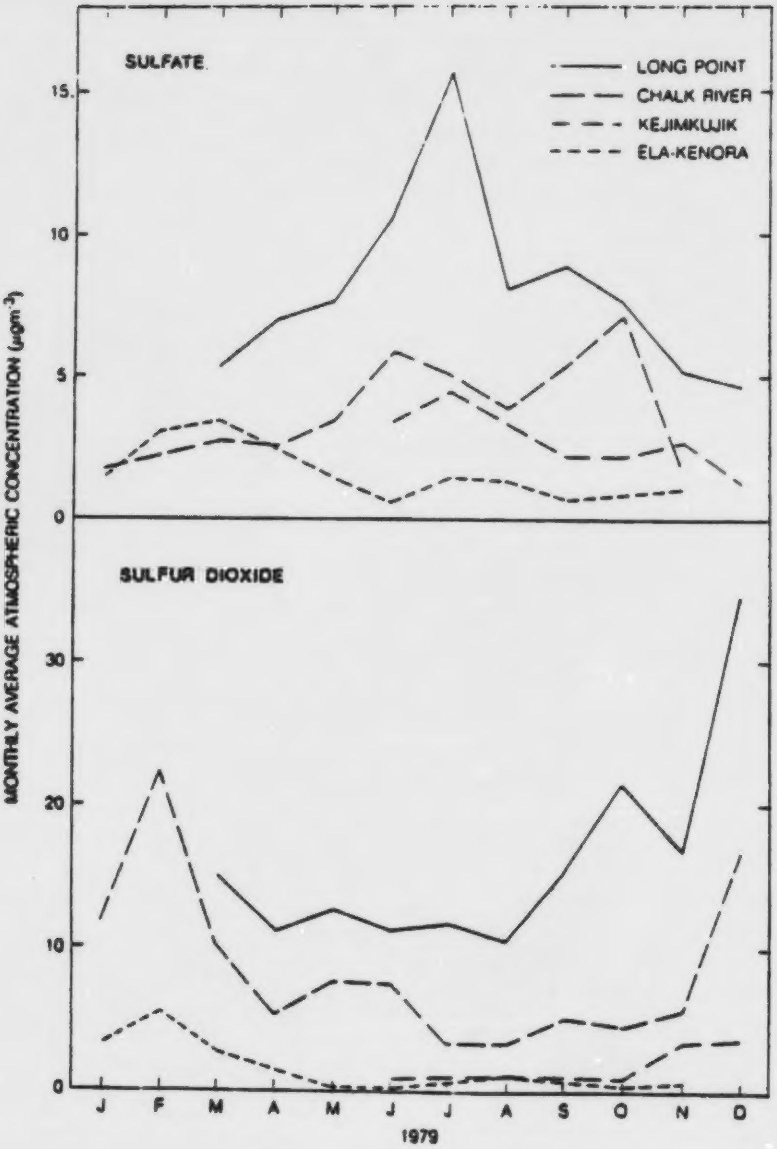


Figure 15. Temporal variations of the monthly average concentrations of atmospheric sulfate and sulfur dioxide at APN sites during 1979 (Barrie 1982).

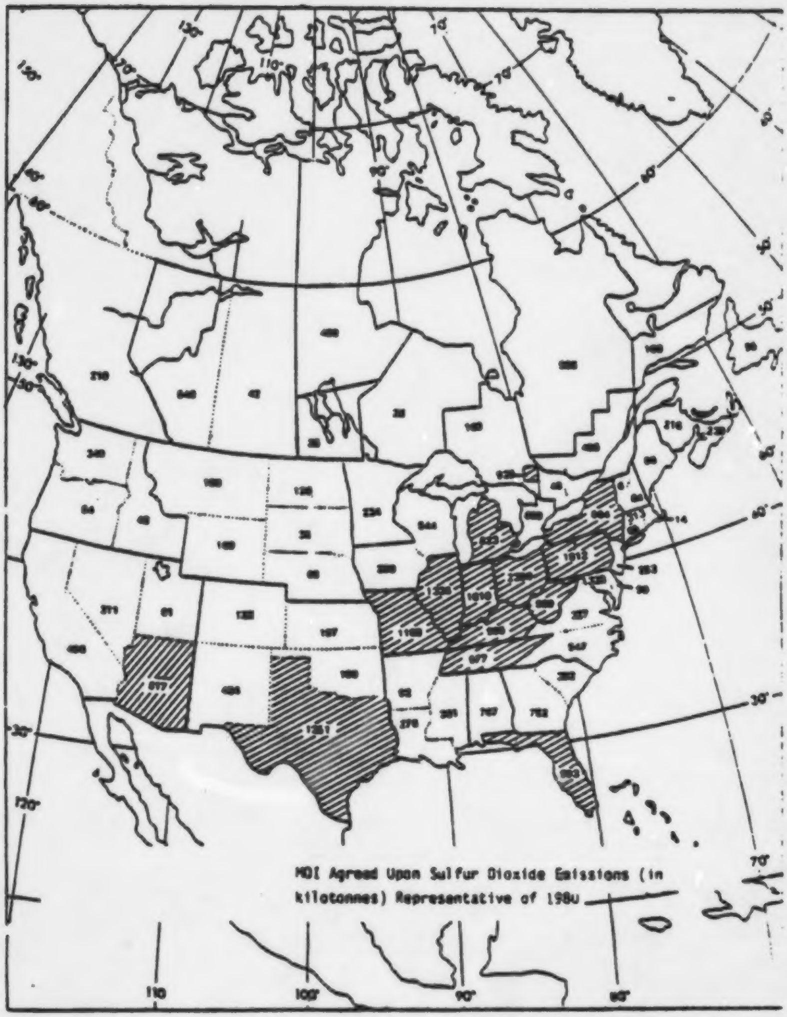
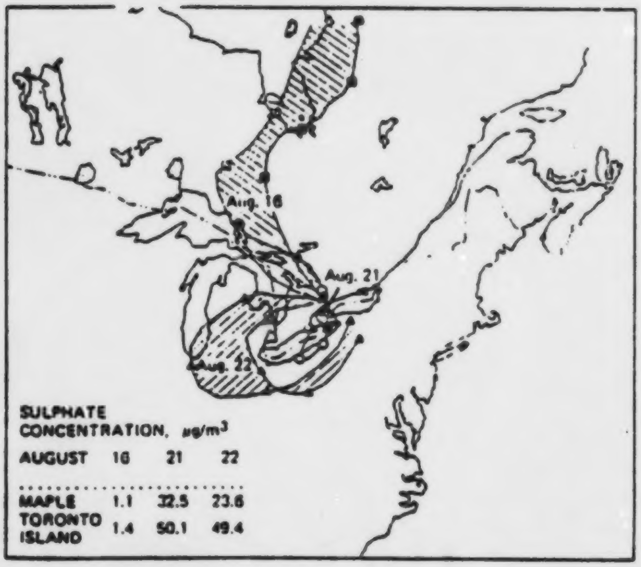

MOI Agreed Upon Sulfur Dioxide Emissions (in kilotonnes) Representative of 1980
210
47
28
340
64
120
234
371
107
1100
1010
1912
977
947
707
762
270
1251
216
14
30
70°
30°
60°
120°
110
100°
90°
80°

Figure 16. Sulfur dioxide emissions inventory for 1980 from MOI-Report 2F-I.



SULPHATE CONCENTRATION, µg/m³

AUGUST	16	21	22
MAPLE	1.1	32.5	23.6
TORONTO ISLAND	1.4	50.1	49.4

Figure 17. Four-day back-trajectories ending at Toronto at 19:00 EST on the dates shown. Full and open symbols represent 85 kPa and 100 kPa trajectories respectively (Anlauf et al. 1980).

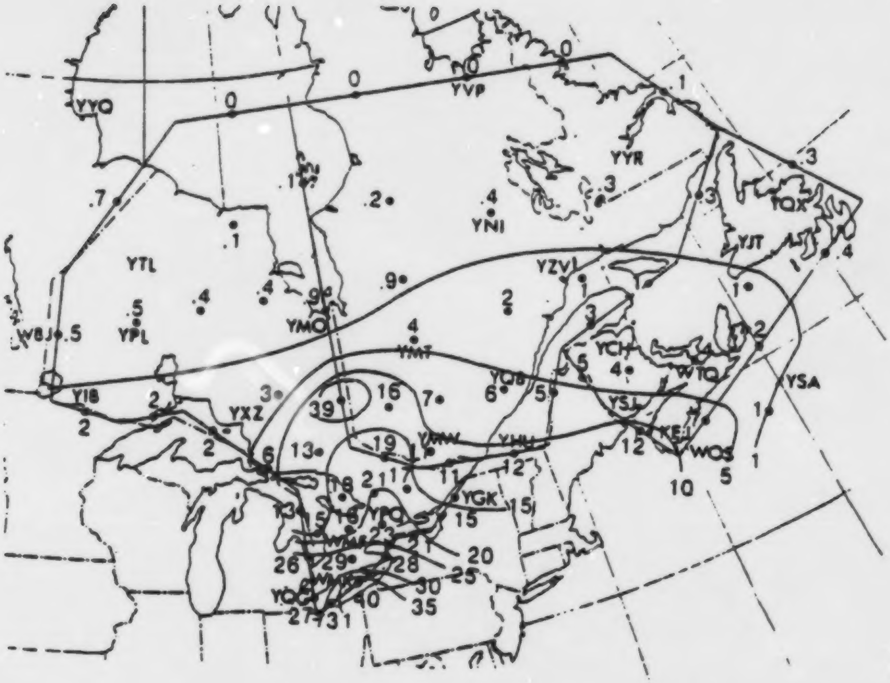

YYQ
YVP
YYR
TQX
YJT
YNI
YTL
YPL
WBJ
YMO
YZV
YMT
YCH
WTQ
YSA
YQB
YSJ
KEJ
WOS
YIB
YXZ
YGK
YPQ
YQG
YHU
39
40
35

Figure 18. Computed 1978 annual average SO_2 concentration ($\mu g\ m^{-3}$) based on full North American emission inventory (Olson et al. 1982). Concentrations may be higher than actual values since emissions may have been overestimated in the available inventory (Olson 1983-personal communication).

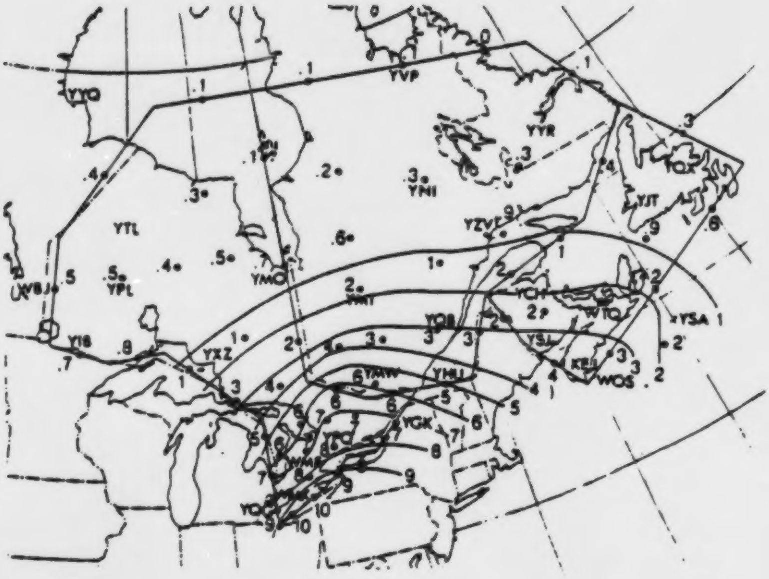

YYQ
YVP
YYR
YNI
YTL
YPL
YBJ
YMO
YZV
YQX
YJT
YCH
WTQ
YSA
YQB
YSL
KEJ
WOS
YXZ
YIB
YMW
YHU
YGK
YOO

Figure 19. Computed 1978 annual average SO_4 concentrations (SO_4^{2-}) based on full North American emission inventory (Olson et al. 1982).

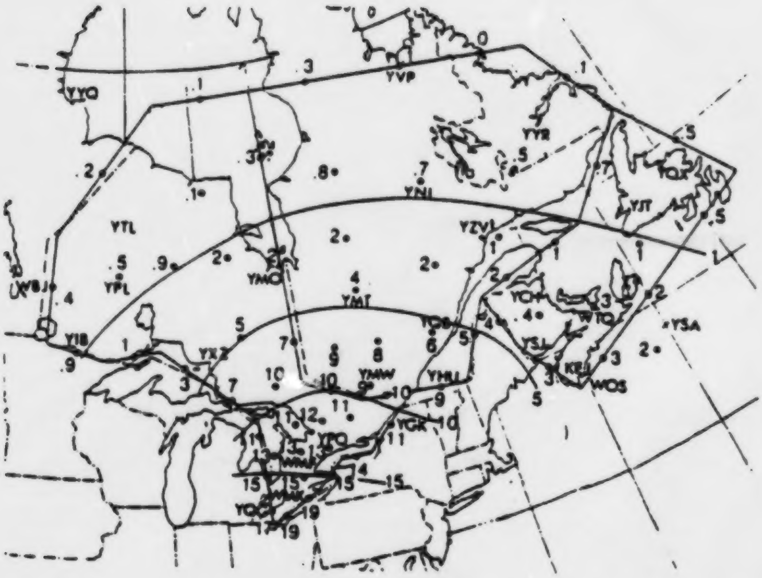

YYQ
YVP
YYR
YQX
YJT
YTL
YPL
YMO
YNI
YZV
YMT
YCH
YSA
YQB
YSJ
YXZ
YMW
YHU
YQK
YQG
WOS

Figure 20. Computed 1978 annual wet S deposition in kg S/ha based on full North American emission inventory (Olson and et al., 1982).

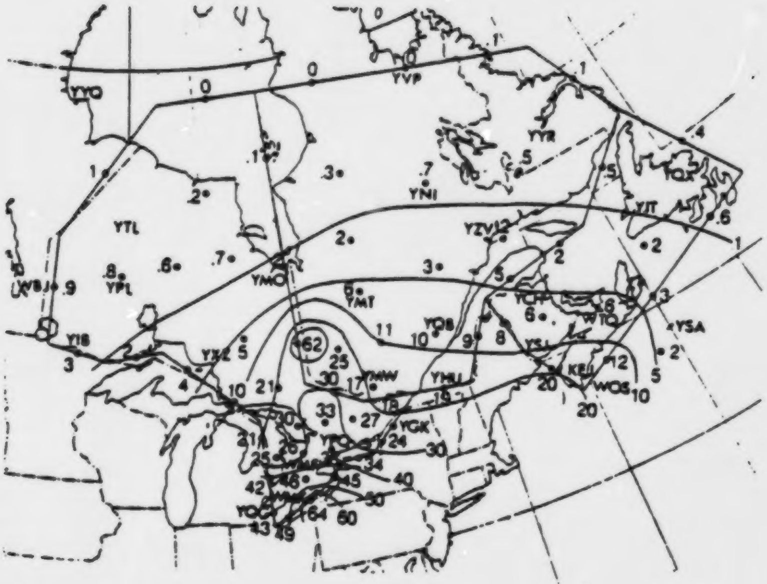

0
.1
YYQ
0
0
YVP
1
YYR
.4
.1
.1
1
.3
.7
YNI
.5
.5
YQX
.2
YIT
.6
YTL
2
YZV
12
1
2
.2
.8
YPL
.6
.7
YMO
3
2
.5
3
.9
YWBJ
6
YMT
YCH
6
.6
YSA
YIB
3
5
YXZ
62
11
10
YQB
9
8
YSJ
12
2
5
25
4
10
21
30
17
YMW
YHU
20
KEJ
WOS
10
20
19
18
33
27
30
YGK
21
YTO
24
30
25
26
34
40
46
45
42
50
YQG
64
60
43
49

Figure 21. Computed 1978 annual dry S deposition in kg S/ha-1 based on full North American emission inventory (Olson et al. 1982).

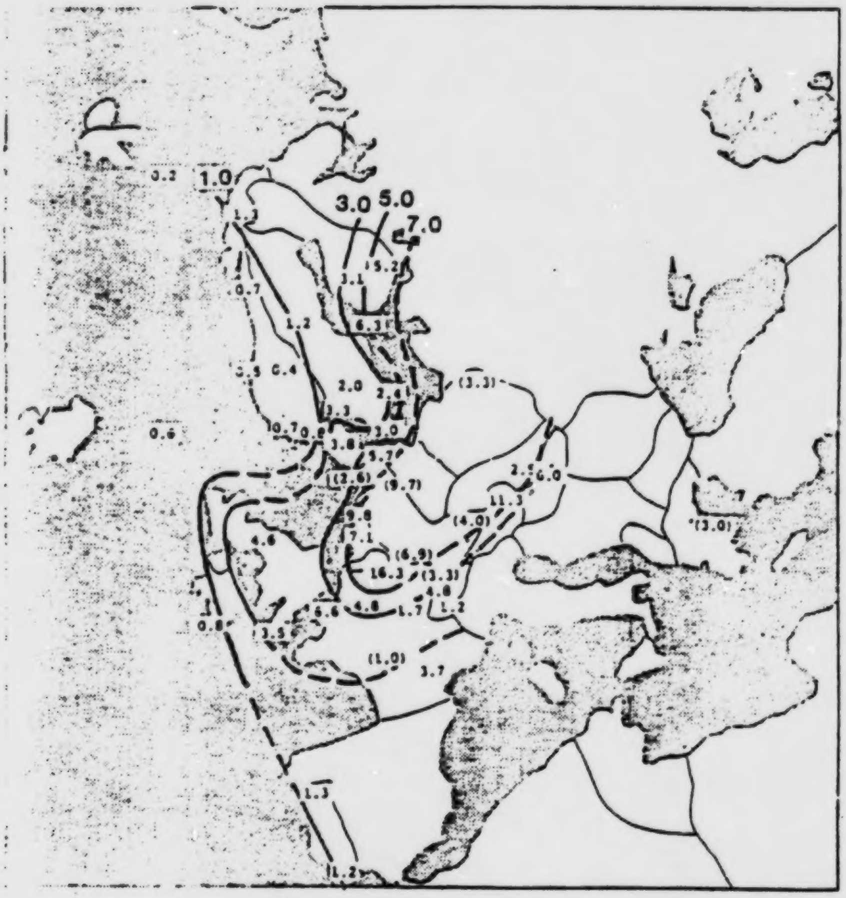

1.0
3.0
5.0
7.0
0.2
0.7
1.2
2.0
(3.3)
0.6
(9.7)
(4.0)
(3.0)
16.3
(3.3)
4.8
(1.0)
3.7
0.8
1.3
1.2

Figure 22. Mean annual sulfur dioxide concentration ($\mu g/m^{-3}$) for 1981 over western Europe (preliminary data EMEP).

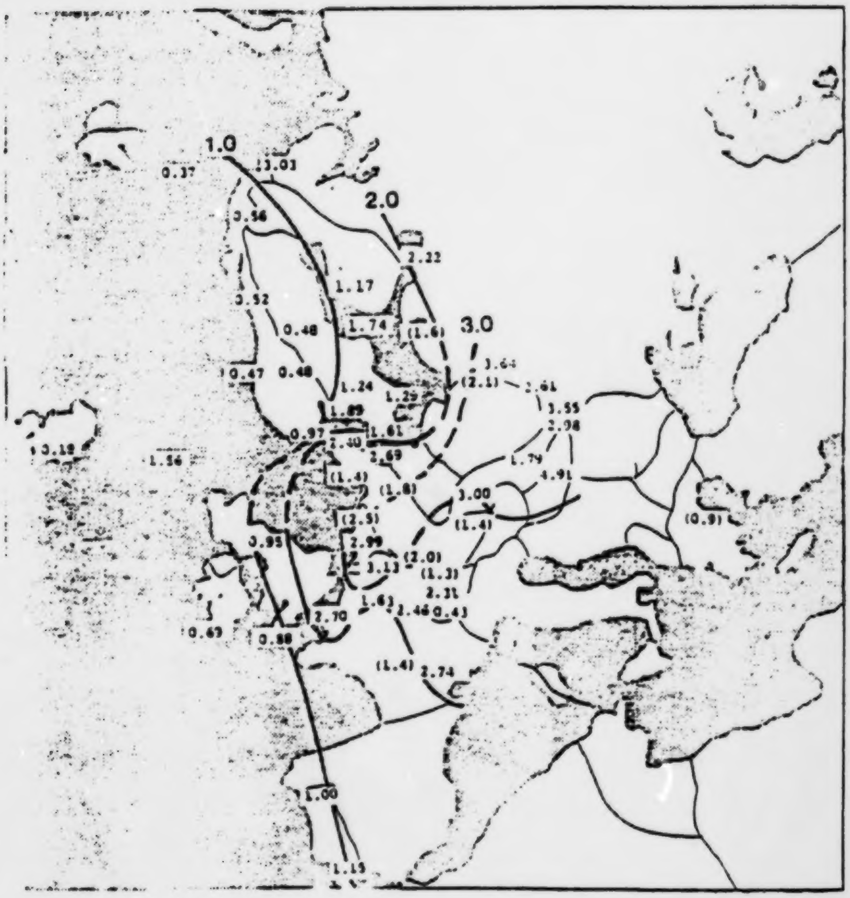

1.0
2.0
3.0
0.37
2.22
1.17
1.74
(1.6)
0.48
0.47
0.48
1.24
1.29
(2.1)
3.55
2.98
1.56
0.97
2.40
1.61
2.69
1.79
4.91
(1.4)
(1.8)
3.00
(1.4)
(2.5)
0.95
2.99
(2.0)
(1.3)
2.31
1.63
2.46
2.70
0.63
0.88
(1.4)
2.74
(0.9)
1.00
1.15

Figure 23. Mean annual sulfate concentrations (μg/m-3) for 1981 over western Europe (preliminary data EMEP).

TECHNICAL SESSION II
EFFECTS OF ACID RAIN ON FOREST VEGETATION

Effects of Acid Rain On Forest Vegetation: Morphological and Non-mensurational Growth Effects

Kevin E. Percy
Canadian Forestry Service

ABSTRACT

Acid rain is widely perceived to be a threat to forest resources in eastern Canada. The majority of rainfall events in this area have a pH of 4.0-4.5 with most of the more acidic events occurring during the active growing season. Although field injury has yet to be documented, experimental evidence with seedling-stage plants suggests that direct damage to forest tree species can be induced under controlled conditions using simulated rainfall techniques. Seed germination can be inhibited, but usually only at extreme rainfall acidities. Inhibition is generally more severe in deciduous species than in coniferous. In contrast, seedling growth and development can be affected by near-ambient rainfall pHs. Observed morphological effects include reductions in the rates of needle and secondary meristem initiation, and in shoot apex size. Growth effects include decreased height and reductions in hypocotyl, cotyledon and needle elongation. Leaf wettability and rainwater penetration rate through the cuticle may be altered as a result of chemical or physical modifications to leaf surface structure by acidic solutions. Macroscopic leaf injury has not been detected at simulated pHs above 3.4. Little is yet known about cellular or sub-cellular effects. Preliminary species-sensitivity data are available, but interspecific variation in seedling response is large, and further work is required before extrapolation to the field situation can be made.

INTRODUCTION

Much of the precipitation falling on eastern North America is acidic (pH <5.6). It has been estimated that acid rain currently impinges on 800 000 ha of forest land in the United States (Jacobson 1980) and, in Canada, on about 6 000 000 ha of forest land in the province of Quebec alone. Although the concentrations of inorganic ions in the rain are relatively dilute, the weighted mean annual pH of rain in eastern Canada and in the northeastern United States lies between 4.0 and 4.5 (Bangay and Riordan 1983). Of particular concern to the forestry sector is the occurrence of the most acidic rain events during the active growing season of north temperate forest tree species. A measure of the potential economic impact from a reduction in forest growth caused by acid rain is indicated by the fact that, in 1981 alone, the total sales value of forestry goods in Ontario, Quebec, and the Atlantic provinces, the area of the country receiving acid rain, exceeded $13 billion.

Among wet-and dry-deposited pollutants affecting forest vegetation, acid rain has received the most attention lately. However, other air pollutants currently crossing national and international boundaries are potential agents of injury. These include oxides of sulfur (mainly SO_2), oxides of nitrogen (mainly NO_2), oxidants (O_3), particulates, and heavy metals. These pollutants may occur singly, or more commonly in combination, over large areas of forest land. Damage to forest vegetation occurs through direct contact with vegetative and reproductive structures of plants or indirectly through an initial effect on the physical, chemical, and biological characteristics of the soil. The purpose of this paper is to review the current state of knowledge on the direct effects of acid rain on the morphological characteristics and growth of forest trees.

POLLUTANTS OF CONCERN

Sulfur Dioxide

Sulfur dioxide (SO_2) is a primary pollutant, emitted in phytotoxic concentrations from a wide variety of anthropogenic sources such as thermal electric generating stations and non-ferrous smelters. It is the pollutant which has received most attention over the past 50 years, and many reviews dealing with its effects on vegetation are available (Linzon 1978; Mudd 1975; Rennie and Halstead 1977; Treshow 1970). Classic, long-term studies such as those around Sudbury (Linzon 1978) have documented chronic effects on forest growth when SO_2 concentrations averaged about 43 $\mu g\ SO_2\ m^{-3}$. Acute foliar injury has been induced under laboratory conditions at concentrations of 770 $\mu g\ SO_2\ m^{-3}$ over two hours (Berry 1971; Evans and Miller 1975; Houston 1974; Karnosky 1976; Smith and Davis 1977, 1978). Some studies have documented hidden or latent foliar injury at lower concentrations, but anatomical or physiological changes were not usually accompanied by growth loss (Eckert and Houston 1980; Keller 1977; Percy and Riding 1981).

Average concentrations of sulfur dioxide in the northeastern United States have been estimated to average 16 $\mu g\ m^{-3}$ annually (Shinn and Lynn 1979). Concentrations in eastern Canada averaged 5-10 $\mu g\ m^{-3}$ monthly during 1980-81 (Barrie et al. 1982). Sulfur dioxide alone, therefore, cannot be considered to be an important phytotoxicant on a broad regional scale. However, its interactive role with other pollutants (such as acid deposition) in causing direct injury to vegetation is yet to be clarified.

Ozone

Photochemical oxidants are the most widespread air pollutants causing direct injury to forest vegetation. Ozone (O_3) is the oxidant that has generated the most concern because of its strong phytotoxic potential and its occurrence at considerable distances downwind of major urban centres. There are several excellent reviews available on the direct effects of O_3 on forest vegetation (Heath 1975; Skelly 1980), many of the most important native tree species are considered susceptible (Davis and Wilhour 1976). Concentrations as low as 196 $\mu g\ O_3\ m^{-3}$ for six hours per day are known to induce growth reductions in sensitive species (Wilhour and Neely 1977).

Ozone concentrations in at least two forested areas in the southwest and northeast United States, where average monthly concentrations range from 78-127 $\mu g\ m^{-3}$, have caused direct injury to sensitive tree species, and reduced the productivity of seedling, grown in open-top chambers supplied with ambient air (Skelly 1980). Ozone concentrations in these areas and in southern Ontario are episodic in occurrence. Data gathered at rural monitoring stations along the United States border during 1976-81 (Bangay and Riordan 1983) indicate frequent incidents of elevated, potentially phytotoxic, ozone concentrations during the growing season. Ozone should, therefore, be considered in any regional-scale evaluation of the direct effects of air pollutants on forest vegetation, particularly in southern Ontario and over much of the northeastern United States.

Pollutants in Combination

Air pollutants, rarely encountered singly in the field, are more commonly found in combination. For instance, measurable concentrations of sulfur dioxide and low concentrations of ozone occur concomitantly with acid rain events over much of the current impingement zone of long-range transported air pollutants. Interactions among these pollutants could conceivably result in an enhancement, or reduction, of direct injury to forest vegetation over the amount expected from exposure to only one pollutant. Some research results are available on the effect of a combination of sulfur dioxide and ozone on the growth of forest trees (Jensen 1981; Yang et al. 1982). The interactive effects generally have been variable, and dependent upon a range of environmental and pollutant dose factors. No results, however, are available on the interactive effects of gaseous pollutants and acid rain on forest vegetation, although a few such studies have been completed on agricultural crops (Irving and Miller 1981).

Further research is required into the effects of pollutants in combination on forest vegetation. Other air pollutants such as oxides of nitrogen and particulates, though of local interest, are currently not of major importance on a regional scale and will not be considered in this paper. There is also increasing concern over a long-term accumulation of heavy metals in forest ecosystems in the northeast (Johnson et al. 1982; Lindberg and Harriss 1981). However, the potential effects of such metals on forest vegetation are likely to occur indirectly, through an alteration of soil chemical or biological conditions.

ACID DEPOSITION

Potential Effects and Influencing Factors

The general effects of acid rain on vegetation have recently been reviewed by several authors (Evans 1982; Jacobson 1980), and the specific effects on forest trees have been outlined in the Phase III report of the Memorandum of Intent (MOI) document (Bangay and Riordan 1983) and in a report by the National Council of the Paper Industry for Air and Stream Improvement (NCASI 1983). There is at present no evidence of direct injury from acid rain alone to forest trees in the field, under either ambient or artificial conditions. However, experimental evidence from simulated rain laboratory studies with seedling stage plants indicate that there may be many potential direct effects on sensitive species, or alternatively on less sensitive species during susceptible stages of their life cycle.

A list of theoretical direct effects of acid precipitation on vegetation was first proposed by Tamm and Cowling (1977). These included damage to the protective surface structures of plant leaves, such as epicuticular or surface waxes, and the underlying cuticle; interference with the normal functioning of guard cells which regulate gaseous exchange between plant leaves and the atmosphere; poisoning of plant cells, such as epidermal cells, following diffusion of acidic substances through stomata or the cuticle to produce chlorotic or necrotic discolorations on leaves or branches; disturbance of normal cellular metabolism or growth processes without cell death or necrosis, resulting in abnormal development or premature senescence of plant parts; alteration of leaf- and root-exudation processes leading to changes in populations of leaf and root surface microorganisms; interference with reproductive processes; and synergistic interaction with other environmental stress factors. Most of these theoretical effects have been subsequently confirmed by laboratory research.

There are many biotic and abiotic factors that interact to determine the direction and degree of plant response to the direct effects of acid rain. These factors could include some of the following: species sensitivity (variation between species (Percy 1983) and variation within clones of a single species (Evans et al. 1978) — large for both coniferous and deciduous species); stage of plant development (recently established seedlings have been shown to be more sensitive than older material (Wood and Bormann 1974)); physiological age of the receptor foliage (leaf age has affected susceptibility in several agricultural and forest species (Evans et al. 1977, 1978; Evans and Curry 1979)); time of year of the rain event or events; and plant vigor at the time of treatment. All other factors which may influence plant response interact to determine the dose variable in the dose-response equation. These could include the acidity or pH of the precipitation; the chemical composition of precipitation; the intensity of precipitation; and the frequency of precipitation events.

Experimental Approaches

The experimental approaches used to investigate the direct effects of acid precipitation on forest tree morphology and growth are listed in Table 1. Various exposure systems were used, rain chambers being most common. Most laboratories used four to six pH treatments, ranging from a control rain of pH 5.6 or 5.7, to a pH 2.7-2.6 for the most acidified rain. As can be seen, a great range of application intensities and frequencies have been utilized. All techniques are modifications of two original approaches developed at Oak Ridge National Laboratory (Shriner et al. 1977) and in the SNSF Project (Abrahamsen et al. 1975) in Norway during the early to mid 1970s. The former approach permits experiments to be conducted in the greenhouse or the field, using portable rain chambers. Environment-rain chambers (Percy 1983), a further refinement, allow for year-round replication of temperature, humidity, and photoperiod in a controlled laboratory setting. Rainfall is applied using specially designed rain nozzles producing regulated rainfall intensities and raindrop diameters (Evans et al. 1977; Percy 1983). The simulated rain solutions used are representative of ambient rainfall with major and minor inorganic ions present in realistic concentrations. The solutions are acidified using both sulfuric and nitric acids, to retain a near-ambient sulfate: nitrate ratio, although this was not always the case in earlier experiments.

The second approach involves the spray-irrigation of established seedlings under field conditions. This allows for a more natural treatment in that seedlings are grown under field conditions and can receive ambient rain alone, ambient rain plus simulated rain, or simulated rain alone. The simultaneous field plot exposure to ambient rain alongside covered field plots receiving simulated rain has also been used recently with agricultural crops.

No single technique is adaptable to all purposes for which the experiments were designed, and each has its advantages and limitations. Results must, therefore, be judged in light of the methodology used.

Table 1. Techniques used to study direct effects of simulated acid precipitation on forest tree morphology and growth

Vegetation tested	Exposure system	Simulated rain treatment			Laboratory Reference
		pH range	Intensity	Frequency	
3 conifers 1 hardwood	Field spray-irrigation	6.0-2.0	0,25,50 mm per event	once per month 5 months per year	SNSF Project (Abrahamsen et al. 1975)
1 conifer	Rain chamber	5.6-2.0	7 mm h^{-1}	one 6-h event per wk	Yale University (Wood and Bormann 1977)
1 hardwood	Laboratory or field rain chambers	6.0-2.3	30 mm h^{-1}	6 or 3 events per wk	Oak Ridge National Laboratory (Shriner 1976)
2 hardwoods	Rain chamber	5.7-2.3	7.2 mm h^{-1}	one 6- or 20-min event per day	Brookhaven National Laboratory (Evans et al. 1977; Evans and Curry 1979)
3 conifers 8 hardwoods	Rain chamber	5.6-2.5	2.5 mm h^{-1}	three 3-h events per wk	EPA - Corvallis (Lee and Weber 1979)
1 conifer 6 hardwoods	Application of individual droplets	2.5-0.5	0.013 - or 0.01- mL droplets	single application	University of Georgia (Haines et al. 1980)
2 conifers 3 hardwoods	Seed germination Container	5.6-3.0	100 mL per irrigation	3 irrigations per wk	State University of New York
1 hardwood	Rain chamber	5.3-2.4	ca 50 mm h^{-1}	one 20- to 30-min event per wk	(Raynal et al. 1982a)
4 conifers	Environment rain chambers	5.6-2.6	5 mm h^{-1}	two 1-h events per day	Maritimes Forest Research Centre (Percy 1983)

EFFECTS ON MORPHOLOGY

Macroscopic Injury

Foliage is the first point of contact between the tree and acid precipitation. In laboratory experiments, simulated acid rain has been shown to induce necrotic lesions on the foliage of many coniferous and deciduous species. The threshold for visible or macroscopic foliar injury typically lies in the range pH 2.5-3.0 (Table 2).

Table 2. Maximum pH of simulated acid precipitation causing direct macroscopic foliar injury to forest vegetation

Species	pH	Effect	Reference
Sugar maple	3.0	Necrotic spots	Wood and Bormann (1974)
Scots pine European white birch	2.0-2.5	Foliar lesions	Abrahamsen et al. (1976)
Scots pine Eastern white pine	2.7	Candle necrosis Needle necrosis	Wood and Pennypacker (1976)
Eastern white pine	2.3	Necrotic segments	Wood and Bormann (1977)
Hybrid poplar (6 clones)	2.7-3.4	10% leaf area with lesions	Evans et al. (1978)
Pin oak	2.5	1% leaf area injured	Evans and Curry (1979)
Eastern white pine 6 hardwoods	1.5	Necrotic spots	Haines et al. (1980)
Norway spruce (2 clones)	2.5	Yellowish appearance	Ogner and Tiegen (1980)
Sugar maple	2.4	Foliar lesions, leaf tip-margin distortion	Raynal et al. (1982b)
Red spruce White spruce Red pine Jack pine	2.6	Lesions, tip necrosis	Percy (1983)

It is apparent from the experiments listed here that several factors influencing plant response to simulated acid rain are of major importance. Tissue age appears to be a determining factor in plant sensitivity. Leaves that are actively elongating or have recently elongated appear to be more sensitive; fully expanded, older leaves are considered to be more resistant (Evans et al. 1978; Evans and Curry 1979). For instance, 14-day-old birch seedlings have been shown to be much more sensitive than six-week-old seedlings (Wood and Bormann 1974). The amount of leaf area exposed also appears to be important. Evidence exists for a linear relationship between the amount of injury measured and the hydrogen ion concentration in the rain (Evans 1982). In coniferous species, the injury usually takes the form of individual lesions, as was observed on expanding spruce (*Picea* sp.) and pine (*Pinus* sp.) cotyledons and primary needles (Percy 1983). As the injury progresses with successive rainfalls, tissue necrosis and deformation (due to internal cellular damage) increase and relatively large areas collapse. Tip necrosis may also occur, leading to a cessation of cotyledon or primary needle elongation. Several consecutive rain events are required to produce such injury, and there is little evidence for foliar damage from isolated events (Evans and Curry 1979; Percy 1983).

There is increasing evidence that the wettability of leaf surfaces may be one of the most crucial factors determining plant response to acid rain. Wettability is a function of leaf morphology, leaf orientation, and the physical and chemical characteristics of surface waxes (Martin and Juniper 1970). The amount of surface wax on a leaf and its structure could conceivably influence plant response because specific areas of the cuticle more frequently allow penetration of the phytotoxic components of simulated acid precipitation (Evans 1982). The removal of surface waxes is known to increase wettability of the leaf surface (Fogg 1948). Although there is contradictory evidence, at the moment, regarding a direct reduction in the amount of surface wax on mature needles due to simulated acid rain (Horntvedt et al. 1980; Lang et al. 1978), gaseous air pollutants are widely known to modify the structure of surface waxes in conifers (Cape 1983; Percy and Riding 1979).

The density and morphology of specialized structures such as trichomes or glandular hairs on leaf surfaces may also be important in determining the initial degree of foliar injury, although other adaxial leaf characteristics may also play a role after repeated rainfalls (Evans and Curry 1979). These structures are prominent in many deciduous tree species and, along with other characteristics such as epidermal cell morphology, may partly explain the hypothesized greater sensitivity of deciduous species relative to than of coniferous species (Evans and Curry 1979). Deciduous species appear to be more easily injured in simulated acid rain experiments that coniferous species, although less research has been completed on the latter group.

The principal pathway of solution entry into the leaf appears to be through the cuticle. Penetration through the stomata is thought to be relatively unimportant (Evans 1982). Cuticle thickness and its chemical composition are, therefore, important in the control of penetration rates. Although there are not likely to be any direct effects of acid rain on the cuticle itself, studies on bush beans indicate that the selective penetration characteristics of inorganic ions and the interaction of solution acidity with these characteristics may be critical in determining individual species response (Evans et al. 1981).

Several authors have suggested relative sensitivities of vegetation based on degree of macroscopic injury (Evans and Curry 1979; Evans 1980). The ranking, from highest to lowest sensitivity, is as follows: herbaceous dicots, wood dicots, monocots, and conifers. Recent research at the Maritimes Forest Research Centre (MFRC) has produced the following ranking based on the degree of germination inhibition: red spruce, which is most sensitive, followed in order of decreasing relative sensitivity by white birch, black spruce, balsam fir, white spruce, white pine, jack pine, and red pine (Percy, unpublished data). Sensitivity rankings are influenced greatly by the parameter or parameters upon which the ranking is based, and on other previously discussed factors influencing individual plant sensitivity.

Microscopic Injury

Little work has been completed on the microscopic or cellular-level effects of simulated acid rain on forest trees. Histological studies have been completed with hybrid poplar (Evans et al. 1977) and pin oak (Evans and Curry 1979) at Brookhaven. In six hybrid poplar clones, the percentage of leaf area with lesions, and the percentage of leaves injured, increased with decreasing rain pH. There were differences, however, in cellular effects. Abnormal cell enlargement and proliferation were induced to various degrees, depending upon intraspecific sensitivity within the six clones tested.

Characteristics of the adaxial (upper) leaf surface and epidermal cell morphology during leaf development were two anatomical characteristics hypothesized to predispose leaves to lesion development because injury from acid rain preferentially affects the leaf indumentum near the trichomes and vascular tissues, with the epidermal cells being injured only after many rainfalls (Evans and Curry 1979). It has been suggested from this work that cellular responses of foliage may help reduce macroscopic injury, because foliage manifesting extreme cell enlargement and proliferation generally had fewer lesions. More work is required to define better the processes involved in foliar injury and the relative importance of cellular injury in affecting overall growth response and subsequent plant form.

Effects on Growth

Despite several studies investigating the effect of simulated acid rain on the growth and productivity of agricultural crop species (Jacobson 1980), there are few studies dealing with such effects on forest vegetation. However, among these studies there is general agreement that certain stages of the plant life cycle are particularly susceptible. With woody species, seed germination, seedling establishment, and the first growth cycle are among the most susceptible. Therefore, most of the research has concentrated on effects during these stages.

The effect of simulated acid rain on forest tree seed germination and seedling emergence is summarized in Table 3. Early work in Norway (Abrahamsen et al. 1975) with acid additions to mineral soil showed an optimum pH of 4.8 for germination, with a marked inhibition of germination and establishment recorded at pH <4.2. Only 20% of the seeds developed normally at pH 3.8. Lee and Weber (1979) used rain chambers to apply simulated rain at four pHs to seeds of 11 woody species. They observed considerable variation in the direction and magnitude of the interspecific responses. Emergence was inhibited in only one species, sumac (*Rhus* sp.), at a pH of less than 5.7, although emergence in four species was stimulated. No effect was detected on the emergence of six others. In another study using seeds grown in acidified substrates, inhibition of germination was measured at pH 4.0 in red maple (*Acer rubrum* L.) and at 3.0 in yellow birch (*Betula alleghaniensis* Britt.) (Raynal et al. 1982[a]). Germination of sugar maple (*Acer saccharum* Marsh.) and eastern hemlock (*Tsuga canadensis* L.) was not affected, although germination was stimulated in eastern white pine (*Pinus strobus* L.) with decreasing pH.

Seed germination in two conifers examined was inhibited at pH 2.6 in a study at MFRC (Percy 1983). The seeds were sown in a forest organic soil, germinated in environment-rain chambers under optimum germination conditions, and exposed to the average 1980 growing season rainfall amount and chemistry adjusted to the appropriate pH with H_2SO_4:HNO_3. Significant inhibition of both germination and seedling establishment at pH 2.6 was recorded in red spruce (*Picea rubens* Sarg.) and white spruce (*Picea glauca* (Moench) Voss.), with no effect measured on jack pine (*Pinus banksiana* Lamb.) and red pine (*Pinus resinos* Ait.). Additional data showed significant inhibition in black spruce (*Picea mariana* (Mill.) B.S.P.), balsam fir (*Abies balsamea* (L.) Mill.) and white birch (*Betula papyrifera* Marsh.) and no discernible effect on eastern white pine (Percy, unpublished data).

From the limited number of studies available it is apparent that simulated acid rain can affect seed germination capacity and that seedling establishment is perhaps even more sensitive (Percy 1983). The direction and amount of response, however, appear to be greatly influenced by experimental methodology.

Table 3. Effect of simulated acid precipitation on forest tree seed germination

Species	Response[a] Inhibition	No effect	Stimulation	Reference
Norway spruce	X			Abrahamsen et al. (1975)
Scots pine	X			
Douglas fir			X	Lee and Weber (1979)
Eastern white pine			X	
Eastern red cedar			X	
Flowering dogwood		X		
Staghorn sumac	X			
Red alder		X		
Shagbark hickory		X		
Yellow birch			X	
Sugar maple		X		
American beech		X		
Tulip poplar		X		
Sugar maple			X	Raynal et al. (1982a)
Red maple	X			
Yellow birch	X			
Eastern hemlock		X		
Eastern white pine			X	
Red spruce	X			Percy (1983)
White spruce	X			
Red pine		X		
Jack pine		X		

[a] Response measured at one or more acidified rain pHs.

Seedling growth and form as affected by simulated rain have received only slightly more attention. No effect on yellow birch seedling growth was induced by Wood and Bormann (1974) with an acidified, pH 3.0, mist. Treatment with pH 2.3 was required to produce significant growth reduction (Table 4). In a subsequent study (Wood and Bormann 1977), short-term productivity of eastern white pine seedlings was promoted as the concentrations of sulfuric, nitric, and hydrochloric acids were increased in the rain. Total plant weight, needle weight, and needle length were greater after 20 weeks of rain at pH 3.0 than at pH 5.6. The authors cautioned, however, that this increase in productivity may have been only a short-term phenomenon. In another study, no inhibition in above-ground dry weight was measured in any of the 11 woody species, although growth was stimulated in four species (Lee and Weber 1979). The root dry weight was inhibited in one species and was unaffected in the other 10. Over a three-year period rooted cuttings of two clones of Norway spruce were irrigated with a multielement solution acidified with sulfuric acid (Ogner and Tiegen 1980). No harmful effects were detected, and the trend was towards a slightly increased growth rate due to acid treatment. The authors concluded, therefore, that Norway spruce has a toxic tolerance provided that nutrient elements are available in sufficiently high concentrations.

Table 4. Effect of simulated acid precipitation on forest tree growth

Species	Response[a]			Reference
	Inhibition	No effect	Stimulation	
Yellow birch	X			Wood and Bormann (1974)
Eastern white pine			X	Wood and Bormann (1977)
Douglas fir		X		Lee and Weber (1979)
Eastern white pine		X		
Eastern red cedar		X		
Flowering dogwood		X		
Staghorn sumac		X		
Red alder		X		
Shagbark hickory			X	
Yellow birch		X		
Sugar maple			X	
American beech	X			
Tulip-poplar			X	
Norway spruce			X	Ogner and Tiegen (1980)
Sugar maple	X		X	Raynal et al. (1982b)
Red spruce	X			Percy (1983)
White spruce	X			
Red pine	X			
Jack pine	X			

[a] Response measured at one or more acidified rain pHs.

Radicle elongation may be more sensitive to the direct effect of acid rain as was shown in a study with sugar maple (Raynal et al. 1982b). Elongation was reduced up to 37.5% and 60% following exposure to pH 3.0 and 2.4 treatments, respectively. Seedling growth response was variable depending upon the capacity of the soil to supply nutrients, and both inhibitory and stimulatory effects were observed.

Direct effects of simulated acid rain on several important morphological and growth parameters are being measured in studies in progress at MFRC (Percy, unpublished data). Hypocotyl elongation was affected by acid rain application in all seven species tested. Length was inhibited at pH 4.6 in red spruce, black spruce, and red pine; at pH 3.6 in jack pine and balsam fir; and at pH 2.6 in white pine and white spruce. The number of primary needles initiated was inhibited in white spruce, red spruce, and red pine at pH 4.6, and in the other four species at pH 2.6.

The effect of simulated acid rain on the initiation of axillary or secondary meristems was more variable. Inhibition at pH 2.6 was common in all species on which meristems were observed. The responses at pH 4.6 and 3.6 ranged from stimulatory to inhibitory and were species dependent. Shoot apex height was more consistently affected by rain pH. Apex height was reduced at pH 4.6 in three species and at pH 3.6 in the two other species among the five evaluated thus far. These data indicate a potential direct effect of eastern Canadian rain on the morphology and growth of seedlings of major forest tree species.

SUMMARY

Research into the direct effects of acid rain on vegetation has gained much attention during the past few years. In this paper, a review of the current knowledge regarding these effects as they pertain to the morphology and growth of forest vegetation has been presented. At present, there is no conclusive, unequivocal field evidence for a direct effect of ambient rain on forest growth, although acid rain and air pollutants in general have been much discussed as contributing to forest declines or growth reductions in forests in the United States and Europe (Johnson and Siccama 1983; Johnson et al. 1981; Jonnson and Sunberg 1972; Puckett 1982; Tomlinson 1983).

The data presented here suggest that the direct interaction between acid rain and plant foliage can alter the morphology and growth of seedlings of many forest tree species. However, there are many factors that may determine plant response to isolated extremely acid events, or alternatively to a succession of less acid ones. While current knowledge has added to an understanding of the process of direct injury, numerous questions remain unanswered. Laboratory studies should not be taken out of the context in which they were performed and applied to the field in either a predictive or a quantitative manner. Rather, they should be regarded as indicators of specific potential effects that could occur in the field under certain conditions. Serious consideration should also be given to the inclusion of combinations of pollutants in experiments when possible and applicable. Well-designed field experiments able to detect subtle effects will need to be established in order to document direct effects in the field, which could then be applied on a wider basis.

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DISCUSSION

Question: Most of the data on the effects of acid rain on vegetation show that the threshold for visible injury or potential metabolic damage is pH 3.5. You found some inhibition of hypocotyl growth and primary needle initiation at pH 4.6. Since the average pH of rain in Ontario at the worst situation is pH 4.1, I am wondering how relevant your data are to the forest situation.

Answer: That is a difficult question to answer. In my experiments, the treatments used involved the average growing season rainfall amount and the 1980 growing season mean rainfall chemistry applied at realistic low rainfall intensities with medium-sized shower droplets. The evidence thus far indicates that a succession of average rain events may induce direct injury to forest vegetation in the laboratory setting. I do not think that the data can be taken further at this stage and extrapolated to the field.

Question: Were there any effects on soils in the Ontario tubes?

Answer: The soil pH and chemistry did not appear to be significantly buffered or altered deleteriously due to the five weeks of treatment with simulated acid rain, although the data have not been fully analyzed yet.

Question: Colleagues in meteorology are concerned about chemical variations within and among rain events. What is their biological relevance? Could you comment on the shortest time in which biologically important harm to forest or agricultural crops has been reported?

Answer: During seed germination in some forest species there is an inhibition of germination rate within days of seed imbibition of acidified solutions, as well as a marked decrease in final germination capacity. There is no evidence for direct injury to seedlings due to isolated rain events. In forest species the shortest time during which direct injury can be induced is perhaps a week or two, if successive events are applied on a daily or every other day basis. For agricultural crop species, Evans has demonstrated that the time required for effects to appear is substantially shorter than for forest tree species. In a matter of days, direct effects are visible. The biological relevance of chemical variation within and between rain events is not understood at this time.

Physiological and Biochemical Effects of Acid Deposition on Forest Vegetation

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ABSTRACT

Despite many mechanisms by which acid deposition might directly damage plants biochemically, none has been documented. Strong acids would ionize to form anions and protons. The hydrogen ions briefly accumulating would first render the cell wall region very acidic. This in turn may alter the calcium balance and cause a loosening reaction of the wall fibers leading to water imbalance. Any buildup of anions might promote osmotic imbalance. Subsequent reactions of hydrogen ions with membranes are possible, and a significant increase in leaching of potassium, magnesium, and calcium ions has been reported following foliage sprays with artificially acidified rain.

Although several important plant processes, including potassium balance, carboxylation, ribosome activity, DNA derepression and protein synthesis, are thought to be influenced by hydrogen balance, hydrogen ions may not penetrate the cell sufficiently to affect these processes. The potential effects are more likely a surface phenomenon.

Cytosplasmic pH values range from about 7.0 to 8.5 and may be controlled by regulation of the number of carboxyl groups. The buffering capacity of the cell is limited to coping only with short-term fluctuations. The biochemical effects of acid deposition depend on the balance of internal processes producing and consuming H^+ ions. Equilibrium can be maintained only so long as the H^+ ions produced can be neutralized. Should H^+ concentrations exceed a certain threshold of tolerance, physiological injury may be expected. This threshold may be related to the capacity of cells to actively extrude H^+ and generally appears to be below pH 3.0 to 4.0.

INTRODUCTION

Exploring the potential effects of acid rain on plants inevitably leads us to ask how they might adversely influence metabolic processes. What is there about acid deposition that might alter the biochemistry of the cell? More immediately, do the chemicals involved enter the cell in toxic amounts?

Despite the years of conjecture and speculation regarding the potential impact of acid deposition on plants, there is still little evidence as to the way in which acidity might directly affect plant metabolism if, indeed, it does (Jacobson 1980). More emphasis has been placed on such possible indirect effects as those on the soil pH, leaf surface pH, microbial activity, release of toxic elements in the soil, nutrient leaching (Mollior and Raynal 1982; Killham et al. 1983), interaction with plant pathogens (Bruck 1983), or on whole organism effects such as production and growth (Lee et al. 1981; Cohen et al. 1981; Johnston et al. 1982).

ACID DEPOSITION COMPONENTS

The principal components of acid rain are generally accepted to be sulfuric acid and nitric acid including, of course, the associated hydrogen ions. In related forms, all are natural components of the cell, so the cell can deal with them when they are present in reasonable concentrations. But what is reasonable? At what concentration do they become harmful? Sulfuric acid, of course, is a major component and comes from SO_2. It is extremely difficult in the field to distinguish the potential adverse effects of acid deposition from the effects of SO_2 or other atmospheric pollutants, let alone the components themselves. Sulfur dioxide is a well-known pollutant in its own right and may be the most harmful component as long as it is present. Over distance and time, though, it is converted to sulfate and H_2SO_4, thus forming a component of acid deposition. Once SO_2 becomes dissolved either in the atmosphere or on the leaf surface, it no longer enters the leaf in the gaseous form. As a liquid, much presumably runs off the leaf, a small portion may pass through the stomata into the leaf, and more may remain on the leaf where it might erode the cuticle.

On the plant the sulfates may dissociate. In solution, SO_2 is active in the form of either sulfite (SO_3^{2-}) or bisulfite (HSO_3^-). Thus the fundamental mechanism in which these species act must be about the same. Some researchers (Ferguson et al. 1978) suggest the toxic components of acid rain are the sulfur compounds dissolved in the rain.

Although it is possible that SO_4^{2-} and NO_3^- may effect plant response (Irving and Sowinski 1980), they are probably not toxic by themselves. Studies of foliar fertilizer application (Gray 1977) indicate that, although nitrate is toxic due to its salt effect creating osmotic imbalance, the concentrations used are far larger than any occurring in acid deposition. Also grains are relatively tolerant of acid rain (Neely et al. 1981) yet are among the most sensitive to SO_2.

This leaves us with the hydrogen ion as the most probable toxic component of acid deposition. Hydrogen ions are involved in virtually every cellular reaction. There is no question that H^+ concentration is critical to normal cell and plant development. The only question is the capacity of cells to maintain the effective pH.

Hydrogen ions are continually being produced and consumed within the cell. Generally, where a metabolic reaction involves H^+, such as in the absorption and metabolism of nutrients, there is a pH dependence of the apparent equilibrium constant. Each enzymatic reaction has an optimal range for activity and, in a general way, we can say that the concentration of free H^+ is controlled by metabolism and transport across membranes.

Acidity is regulated by enzymatic reactions that produce H^+ or OH^-. The ability of cells to transport H^+ inward or outward actively, depending on the acidity of the external environment, may well determine the limits of pH tolerance and the ability to cope with increasing acidity.

Buffering systems are involved in pH regulation, although they may be more an effect than a cause of pH regulation during cell growth (Smith and Raven 1979). Carbon dioxide is a principal waste product of cell metabolism and is formed in every organism. It is always available, and the carbonate-bicarbonate buffer system it involves provides the main buffer of cells. A phosphate buffer system is also available to maintain a pH-stat as discussed by Davies (1973). This provides only a short-term, fine-tuning mechanism, and its capacity is limited. Organic acids provide a third buffering mechanism.

Hydrogen ions are continually being redistributed between cytoplasm and vacuole and among organelles, which further helps balance the acidity. A rather sharp gradient in pH exists across the tonoplast which suggests an active H^+ transport from cytoplasm to vacuoles. This proposed hydrogen ion "pump", though, has its limits. However, it should be noted that a drop in external pH from 8 to 4.6 showed only a drop of 0.2 pH units in cytoplasmic pH (Smith and Raven 1979).

The impact of acid deposition, increasing the extracellular H^+ concentration, presumably would be influenced by the background pH of the cell and its constituents. This can vary tremendously, as reported by Small (1955). Substantial variation in pH occurs both among cell components and among plant species.

Mature, lignified cell walls of characteristic Angiosperms may typically have a pH of about 5.6, but become acidified with age to 4.3 and finally 4.0 or even 3.4. Chloroplasts may range from pH 5.6 to

4.8 in the light, but remain at the most acid in the dark. Cell sap in the cortex and pith of the stem may range from 5.6 to 5.9, but may be as low as pH 4.0 to 4.4 in the root cap. Xylem fibers and vessels attain increased acidity with lignification, dropping from 4.4 to 3.4. Phloem generally is less acid and ranges from pH 4.8 to 5.2 in younger stems and becomes less acid with age. Ranges of pH in Gymnosperms tend to be correspondingly lower. These values are rather general, but provide some idea of the natural spread in pH values in normal tissues and cell components. Unfortunately, corresponding data for plants exposed to acid deposition are limited. The tremendous variation in cellular pH suggests that all cells and organelles may well react quite differently to a change in external acidity.

It seems still more significant to note the considerable variation in pH that occurs because of various other environmental influences. Substantial variation in pH occurs from day to day, with time of day, whether in daylight or dark, time of year, age of tissues, and the soil pH (Small 1955).

ENTRANCE OF TOXICANTS AND THE POTENTIAL IMPACT OF H^+

Hydrogen ions or other components of acid deposition land on the surface of the leaf and must penetrate it be sore exerting a metabolic effect. True, the chemical may be directly toxic to the cuticle and act superficially (Evans et al. 1977), but in this paper we are considering only internal impact.

Studies have shown that when simulated rain is acutely acid, in the pH 2-3 range, the leaf cuticle becomes damaged and epidermal cells collapse and die (Evans et al. 1977). When acid rain enters the surrounding cells, abnormal cell elongation and cell proliferation are observed near the trichomes and stoma. This finding leads us to consider the first of several potential mechanisms of action.

Hydrogen ion extrusion is a central feature of many developmental processes, especially those involving cell enlargement (Rayle and Cleland 1977). In a general way, IAA involves K^+-H^+ exchange plus carboxylation that results in cell wall acidification and decreased intercellular osmotic potential. Enlargement is likely due to the uptake of water into the expanding central vacuole. The increase in osmotic concentration of the cell, and especially the increase in cell wall extensibility (i.e., loosening), make expansion possible. Auxins, hydrogen ions, CO_2, or phytotoxin fusicoccin can cause rapid enlargement.

According to Rayle and Cleland (1977), auxin initiates active acidification mechanisms (e.g., a membrane-bound proton pump) that cause a decrease in the pH solution of the cell wall. Unnatural factors that lower the pH may also activate the enzymes that cause loosening. In any case, the mechanism of cell wall loosening involves the activation of wall-bound hydrolases, e.g., polysaccharide hydrolase, which cleave the load-bearing bonds in the wall.

Presumably, the direct addition of hydrogen ions would initiate the same response. Rayle and Cleland (1977) found that adding hydrogen ions to the optimum of pH 3 shortened the enlargement response period from 15 minutes to one minute. When pH 7 buffer was added, elongation ceased. Furthermore, elongation occurred only below pH 4.5.

The loosening of the cell wall, with the potential to allow sliding of the cell wall fibers, increases the permeability and leads to cell water imbalance. Treatments with such pollutants as NO_2, O_3, NO, HF, SO_2, H_2SO_4, or HCl all increase permeability (Heath 1980).

Inside the cell wall, the hydrogen ion concentration influences the structural relation of protein molecules of the membranes which would more seriously interfere with normal permeability and absorption.

Membrane disruption may help to explain the histological effects of simulated acid rain of pH 2.5 described by Ferenbaugh (1976). Leaves of treated plants had smaller cells, less intercellular space, and smaller starch granules within the chloroplasts. The cell contents had a pH less than 4.0. A potential acid/auxin interaction was proposed. Certain acid-sensitive intermediates and decarboxylation reactions might have been adversely affected by acidification. There was no indication that SO_4 had an adverse effect.

Within the leaf, sulfite and sulfate appear to be transported through the cell wall and membrane, into the cytoplasm and to the chloroplast membrane, where they may be incorporated into the chloroplast thylakoids. Here they may interact at disulfide bonds causing a shift of the enzymes to a more active form. Nitrogen oxides are less toxic as gases, but they, too, form acids and add to the acid components.

Acidity also has been found to affect differentially the foliar absorption of phosphorus compounds (Reed and Tukey 1978). Maximum absorption occurred at pH 3-6, although phosphates were also absorbed readily at pH 2.0, which caused necrosis. It was thought that pH influenced the form of phosphate present in solution. Maximum absorption of KPO_4 was at pH 7-10; $NaPO_4$ was at pH 3-6; and NH_4PO_4 at pH 3-10.

It has been suggested that the key to prospective adverse metabolic effects of acid deposition, once having entered the cell, may lie in the inhibition of key, acid-sensitive enzyme systems (Shriner and Johnson 1981). The period during which root nodule formation was most affected by "rain" of pH 3.2 roughly coincided with the period during which soybean nodule nitrogenase actively began to increase exponentially. One possible explanation was that "rain" treatments resulted in a stress-induced shift in carbohydrate allocation to the detriment of nodule energy requirements. The effects could have been caused by either the hydrogen or sulfate ion, but Walddron (1980), comparing equimolar concentrations of sulfate as H_2SO_4 or Na_2SO_4, concluded that any reduction in nodulation was due to differences in H^+ concentration.

Some adverse metabolic effects appear only at very high H^+ concentrations. Sheridan and Rosenstreter (1973) found that a gradual decrease in chlorophyll a and b occurred between pH 6 and 3, but there was a rapid decline only below pH 3. Oxygen production was unaffected down to pH 2.0. Respiration was relatively unaffected above this.

Perhaps the greatest potential for adverse effects is at the growing points where H^+ concentrations are closely related to growth (Weisenseel et al. 1979). Hydrogen ions seem to leak into growing cells and are pumped out of nongrowing ones. Balance of the natural electric currents, which play a role in differentiation and growth of cells, may be upset by the excess H^+.

Growth Responses

Growth responses to simulated acid deposition have been inconsistent. Although they should reflect any adverse stress from chemical imbalance, effects have been shown to be either lacking, positive, or negative. In some studies, adverse effects are found only at a very low pH, e.g., 2.3 (Wood and Bormann 1974) or with the addition of SO_2 (Irving and Miller 1980). Increases in growth have also been demonstrated, as with cuttings exposed to treatments at pH 2.5 (Ogner and Teigen 1980). This was attributed to increased nitrogen uptake.

Although growth responses at the whole plant level are only indirectly involved in this paper, I should like to present one table that suggests a pH range at which some adverse effects might be expected in the absence of superficial necrosis and, therefore, at which some metabolic response could be anticipated. However, in some studies, necrosis was evident even at pH 4.0.

Results of growth studies, as with dendrological studies, are inconclusive, but an interesting trend is suggested when the available data are compiled. Although both growth stimulation and inhibition were found to occur in studies conducted in the pH 2.5-4.0 range, above pH 3.5 most of the responses were either positive or absent. Below pH 3.4, more responses were negative. When data from the existing studies were tabulated, 7% of the responses above pH 3.5 were negative. In the pH range from 3.0 to 3.4, 23% were negative, and from pH 2.5 to 2.9, 50% were negative. These results are based on studies by numerous researchers using over 30 plant species or varieties (Lee and Neely 1980; Evans et al. 1981; Shriner and Johnston 1981; Johnston et al. 1982; Troiano et al. 1982; Evans 1982; Troiano et al. 1981; Heagle et al. 1982; Irving and Miller 1982; Cohen et al. 1981; Lee et al. 1981; Shriner 1978; Jacobson 1980; Evans and Lewin 1981; Mohamed 1978).

CONCLUSIONS

The sulfate component of acid deposition may be potentially toxic because of its effect as a salt, causing differences in osmotic pressure between the leaf sap and the applied solution (Gray 1977). The deposition rates in precipitation, however, would be far too low to have such an effect. However, Irving and Sowinski (1980) suggest that the positive or negative effects on growth found by some workers may have been due to salt or acid stress from high-ionic-strength solutions. One might also look toward the SO_2, sulfite, or bisulfite intermediates.

Table 1. Plant growth and production responses to simulated acid deposition

pH value	Response[a]			
	Positive	Zero	Negative	% studies negative
3.5 and over	9[b]	19	3	
	5[c]	52	4	
Total	14	71	7	7
3.0-3.4	17	3		
	9	22	8	
Total	9	39	11	23
2.5-2.9	4	2	2	
	0	0	4	
Total	4	2	6	50
2.0-2.4	0	2	0	
	0	0	0	
Total	0	2	0	

[a] Response: Positive refers to production greater than the controls; negative, less.

[b] Field studies.

[c] Controlled environment studies.

We can conclude from available data that adverse metabolic effects might be expected under most conditions from acid deposition of pH 2.0, and under some conditions in the neighborhood of pH

3.0. Above this, the natural buffering mechanisms appear capable of coping adequately. Many enzyme reactions have acid optima of pH 4.5-5.5. But what might be the effect of acid deposition on enzymes with more neutral optima?

The biochemical effects of acid deposition depend on the balance of internal processes producing and consuming H^+ ions. Equilibrium can be maintained only as long as the hydrogen ions produced or absorbed can be neutralized. When H^+ concentrations exceed a certain threshold of tolerance, physiological injury can be expected.

If acid deposition should prove harmful at the metabolic level at ambient concentrations, it would most likely be either by (1) disrupting cell wall integrity, especially in meristematic tissues, (2) disrupting protein components of the cell membrane, or (3) disrupting enzymes most sensitive to low pH.

The direct susceptibility of plant cells to injury by acidic deposition may well be determined by their capacity to actively extrude H^+ and thereby cope with changes in external acidity. The concentrations of sulfate and nitrate, plus the pressure of gaseous pollutants and influences of most every other environmental parameter, may influence this capacity as well as the overall response to acid deposition.

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DISCUSSION

Question:	How is the pH of a cell or cell wall determined?
Answer:	It is usually done with chemical indicators of pH in histological staining. Therefore you get a range of pH, not a precise value. You no doubt noticed that the data shown mostly gave a range, not a specific pH.
Question:	Several posters showed a decline in acidity as precipitation passed through the forest canopy. Could some of the acidity be absorbed by the leaf cells? I should certainly think the acidity would be absorbed as the water goes through the tissues and the individual cells. Could the hydrogen ions be translocated?
Answer:	I really think that the hydrogen is far too reactive to be translocated. As with many other pollutants they react upon contact. Much would react at the cell wall, some would pass to the outer membrane, and some might get to the cytoplasm and into the organelles or the membrane of the organelles. They might get pumped into the vacuole. That I should think would be the extent of it.
Question:	You indicated that the sulfate in acid rain would probably have the same kinds of metabolic influences that have been observed with sulfur dioxide. This presumes that sulfate and precipitation can get to the membranes or organelles after entering the stomata or penetrating to the surface of roots in the soil. Would you comment on the likelihood of sulfate in acid precipitation reaching the membranes or organelle surfaces in which they appear to have important biological effects?

Answer: There has been some recent work to measure what sulfur dioxide gets into the leaf, what the conversion rate to sulfide and bisulfide is because it is the sulfur dioxide within the leaf that is of significance. Of course, what is in the external environment influences what is going to get into the internal environment. It is what is in the cell and what remains that counts. Cells get rid of sulfur dioxide and sulfide by converting it to H_2S then exuding it. If enough is exuded the plant is relatively unaffected. The cells nearest the stomates, the subsidiary cells, would be the most impacted, the mesophyll cells less so. If the sulfur buildup is sufficient, other cells may be affected.

Photosynthesis of Woody Plants: The Impact of Acidic Pollutants, Oxidants, and Heavy Metals

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ABSTRACT

Air pollutants reduce the photosynthetic rate of both deciduous and conifer trees. The reduction varies with the pollutant, the dose, and the plant species. Sulfur dioxide and ozone can cause significant reduction in photosynthesis before visible injury can be observed. The reductions are usually only measurable during the fumigation treatments or immediately afterwards because the photosynthetic rate usually returns to the prefumigation level within 24 hours, if no injury is present.

The mechanism or mode of action by which pollutants reduce photosynthesis is still not completely understood. It appears to involve one or more of the following: 1) modification of stomata activity, 2) degradation of chlorophyll, 3) disruption of cell membranes and chloroplast, or 4) inhibition of enzyme activity.

INTRODUCTION

Photosynthesis is the process by which carbohydrates are manufactured from carbon dioxide and water in the chlorophyll-containing tissues of plants exposed to light. It is the most important physiological process in plants because it is the source of all the organic compounds they require for energy and growth.

Studies spanning a wide range of pollutants and doses have demonstrated that photosynthesis can be adversely affected by atmospheric contaminants. There are excellent reviews on specific air contaminants: on sulfur dioxide by Hallgren (1978) and Ziegler (1975); on ozone by Verkroost (1974); and on fluoride by McCune and Weinstein (1971). Smith (1981) reviews all of the major pollutants. This review concentrates on the impact of acidic pollutants, oxidants, and heavy metals on photosynthesis in woody plants.

AIR POLLUTANTS AND PHOTOSYNTHESIS

Sulfur Dioxide

The impact of SO_2 on photosynthesis has been studied in both deciduous and conifer species. Jensen and Kozlowski (1974) exposed quaking aspen (*Populus tremuloides* Michx.) and white ash (*Fraxinus americana* L.) seedlings to 0.2, 0.5, 1.0, or 4.0 ppm SO_2 for 2 or 4 hours. There was no marked change in photosynthesis immediately after the 0.2 or 0.5 ppm treatment, but there was a slight reduction in photosynthesis at 1.0 ppm and a large reduction at 4.0 ppm. Photosynthesis returned to prefumigation levels within 24 hours. Similar responses have been found with pecan (*Carya illinoensis* (Wangenh.) K. Koch) fumigated with 1 to 3 ppm SO_2 for 2 hours (Sisson et al. 1981).

The response of photosynthesis to SO_2 is influenced by both the concentration of SO_2 and the duration of the exposure. Carlson (1979) studied the impact of SO_2 on photosynthesis of sugar maple (*Acer saccharum* Marsh.), black oak (*Quercus velutina* Lam.), and white ash. After 7 days of intermittent fumigation with 0.5 ppm SO_2 at low humidity and low light intensity, the rate of photosynthesis was 52, 46, and 80% for black oak, sugar maple, and white ash, respectively. After 21 days of intermittent fumigation with SO_2, photosynthesis was reduced to 26, 57, and 93% of the prefumigation rate. There was no visible injury observed on these leaves. Lamoreaux and Chaney (1978) investigated the impact of SO_2 on photosynthesis in maple. The photosynthetic rate of excised leaves of silver maple (*Acer saccharinum* L.) was reduced by 48% after fumigation with 1.0 ppm SO_2 for 45 hours, and by 57% after fumigation with 2.0 ppm for 45 hours.

Conifers generally are more sensitive to SO_2 than deciduous trees, and the photosynthetic rate is affected by smaller concentrations of SO_2. Keller (1977a) exposed grafts of fir (*Abies alba* Mill.) and spruce (*Picea abies* (L.) Karst) to continuous fumigation with 0.05, 0.1, or 0.2 ppm SO_2 for 10 weeks from late April until early June; CO_2 uptake decreased with both an increase in the SO_2 concentration and an increase in the duration of exposure. In fir, prolonged exposure to 0.2 ppm SO_2 caused a reduction of approximately 75% in the photosynthetic rate. Keller (1977a) suggested that the loss in annual increment due to the reduced photosynthetic rate may be substantial.

Keller (1980a) later repeated this work. At 0.05 ppm SO_2, there was no reduction in CO_2 uptake, but treatments with 0.1 and 0.2 ppm SO_2 depressed CO_2 uptake before visible symptoms were observed. Keller found that with the same dose (duration x concentration) concentration is more important than duration. Hallgren and Gezelius (1982) conducted a similar study with 4-week-old Scotch pine (*Pinus sylvestris* L.) seedlings. Fumigation at both 0.07 and 0.14 ppm SO_2 reduced the photosynthetic rate, though it returned to prefumigation levels after treatment.

Studies of the effect of large concentrations of SO_2 on resistant and susceptible Scotch pine and Japanese larch (*Larix kaempferi*) were conducted by Lorenc-Plucinska (1978a, b, 1982). Fumigation with 2.5 ppm SO_2 6 hours per day for 4 days inhibited photosynthesis in both resistant and susceptible detached branches of larch. The longer the branches were fumigated, the greater were the reductions in photosynthesis and the longer the recovery. After fumigation, the resistant selection returned to 80% of its original value after 48 hours, whereas the susceptible selection returned to only 40% of its original value. Similar results were obtained with selections of Scotch pine.

Ozone

There is little information on the impact of O_3 on photosynthesis of woody trees. One of the earliest reports was by Miller et al. (1969). Three-year-old ponderosa pine (*Pinus ponderosa* Dougl. ex Laws.) were fumigated with 0.15, 0.30, or 0.45 ppm O_3 9 hours a day for up to 68 days. After 30 days of fumigation, photosynthesis had been reduced by 10, 70, and 85% respectively. After 60 days, the 0.15 ppm O_3 treatment had reduced photosynthesis by 25%.

Barnes (1972) investigated the impact of O_3 on seedlings of slash pine (*P. elloittii* Engelm.), pond pine (*P. serotina* Michx.), white pine (*P. strobus* L.), and loblolly pine (*P. taeda* L.). The seedlings were fumigated continuously with 0.05 or 0.15 ppm O_3 for up to 18 weeks. In young white pine seedlings, O_3 had little impact on photosynthesis, but photosynthesis was slightly depressed in older seedlings with secondary needles. The 0.15 ppm treatment significantly reduced photosynthesis in 2-year-old white pine seedlings, and had a relatively consistent depressing influence on photosynthesis of slash, pond, and loblolly pine seedlings.

Using white pine trees larger than seedlings, Botkin et al. (1971, 1972) found that the threshold for O_3 suppression of photosynthesis was approximately 0.5 ppm for 4 hours. Above this dose, three classes of O_3 sensitivity were detected. In sensitive trees, a dose of 0.5 to 1.0 ppm O_3 for 10 hours reduced photosynthesis to zero. In trees of intermediate sensitivity, a similar dose reduced photosynthesis by approximately 50%, although in resistant trees there was no reduction in photosynthesis. The suppression in intermediate trees was reversible if an ozone-free period followed fumigation.

Lorenc-Plucinska (1979) detached branches from resistant and susceptible selections of Scotch pine and fumigated them with 1 ppm O_3 6 hours a day for 3 days. Photosynthesis was significantly inhibited in both summer and autumn in the susceptible selections.

Fluoride

Fluoride can affect plants as a gas (HF) or as a particulate (NaF). Keller (1973) studied the impact of particulate fluoride compounds on photosynthesis in 1-year-old birch grafts (*Betula* spp.), 3-year-old Scotch pine seedlings, and 4-year-old Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) seedlings. The particulates caused a significant depression in photosynthesis of the birch grafts, but the reduction of photosynthesis in the other species was not significant in the absence of visible symptoms.

Keller (1977b) also investigated the impact of fluoride on photosynthesis of forest trees by placing potted seedlings at varying distances from an aluminum smelter. Photosynthesis of pine seedlings was particularly sensitive to the smelter emissions. Their photosynthetic rate dropped by more than 40% when the foliar concentrations of fluoride reached approximately 30 $\mu g\ g^{-1}$ of fluoride on a dry-weight basis. The photosynthetic suppression decreased with both increasing distance from the fluoride source and increasing foliar maturity.

A second approach to studying the influence of fluoride on photosynthesis is to grow the seedlings or soak shoots in fluoride solutions. McLaughlin and Barnes (1975) used this approach in investigating the effect of fluoride on detached leaves and needles. The needles and leaves were allowed to take up fluoride from a 10^{-4}, 10^{-3}, or 10^{-2} M NaF solution for 24 hours before photosynthesis measurements were made. They found that photosynthesis of three pine species and five hardwood species was significantly reduced by the 10^{-3} or 10^{-2} M NaF treatment. The pines were more sensitive than the hardwoods, and current-year needles were more sensitive than 1-year-old needles

A less severe treatment than soaking the detached needles or leaves in NaF solution is to water potted seedlings with water containing fluoride. Keller (1980b) watered potted spruce cuttings in quartz sand with a solution containing 100 ppm fluoride. The solution was applied during the winter and early spring until budbreak. The soil with fluoride depressed photosynthesis significantly even though previous-year needles did not show injury. The new needles, however, were killed immediately after flushing.

Particulates and Heavy Metals

Particulates interfere with photosynthesis in a different way than toxic gaseous pollutants. Auclair (1976) determined the effects of particulate matter on growth of forests, which act as dust filters. Photosynthesis was measured on Norway spruce seedlings (*Picea abies* (L.) Karst.) that had been hand-dusted with cement or coal dust. At high intensities of light the dust had no effect on photosynthesis, but at low or medium intensities photosynthesis was reduced. Auclair (1977) extended the study to Scotch pine and poplar (*Populus euamericana*) seedlings but used only coal dust. The results were similar.

Toxicity from heavy metals has been studied by growing seedlings in soils containing the heavy metals or by soaking branches in solutions of heavy metals. Carlson and Bazzaz (1977) grew American sycamore (*Plantanus occidentalis* L.) seedlings in soil containing up to 1000 $\mu g\ g^{-1}$ lead and 100 $\mu g\ g^{-1}$ cadmium. After 90 days of treatment, the photosynthetic rate of seedlings treated with either lead or cadmium was reduced. The addition of cadmium to lead-treated plants did not reduce the photosynthetic rate below that observed for plants treated with lead alone.

The influence of cadmium on silver maple leaves was studied by Lamoreaux and Chaney (1978). After soaking the petiole of leaves in solution of 5, 10, and 20 ppm cadmium for 45 hours, the photosynthetic rate was significantly reduced. The leaves treated with 5 ppm cadmium showed an increase in photosynthesis.

Multiple Pollutants

The impact of two or more pollutants on photosynthesis cannot be predicted from information on how an individual pollutant affects photosynthesis. Carlson (1979) observed that an intermittent fumigation with 0.05 ppm SO_2 or 0.05 ppm O_3 for 7 days reduced the photosynthetic rate of black oak by approximately 48%. If the impact of the two pollutants was additive, the photosynthetic rate of black oak seedlings exposed to both pollutants should be reduced by 96%. However, Carlson found that the rate was reduced by only 44%. Conversely, Carlson (1979) found that an intermittent fumigation with 0.05 ppm SO_2 for 7 days reduced the photosynthetic rate of white ash by 20%, whereas treatment with 0.05 ppm O_3 had no effect on the photosynthetic rate. The photosynthetic rate of white ash seedlings exposed to both pollutants was reduced by 38%, which was approximately twice that expected if the effect of the two pollutants had been additive.

These and similar results by Lamoreaux and Chaney (1978), Keller (1980b), and others suggest that the impact of each pollutant combination on each species must be investigated separately. The possibility of developing a general model to predict the impact of pollutants on growth by their impact on photosynthesis appears very difficult.

MODES OF INFLUENCE OR SITES OF ACTION

The mechanism or mode of action by which pollutants impact photosynthesis is not completely understood. It is probably a complex interaction which includes one or more of the following: 1) modification of stomata activity; 2) degradation of chlorophyll; 3) disruption of cell membranes and chloroplast; 4) modification of respiration; or 5) interference with enzymes and other physiological processes.

Stomata Activity

Stomata provide the main route for entry of CO_2 into the leaves of higher plants, and, by influencing the opening and closing of the stomata, pollutants can indirectly influence photosynthesis. Stomatal openings and closings are caused by change in the difference in turgor between the guard cells or a fall in the turgor of the adjacent cells. Similarly, closure can be caused by a fall in the turgor of the guard cells or by an increase in turgor of the adjacent cells (Majernik and Mansfield 1972).

Biggs and Davis (1980) investigated the influence of 0.3, 0.6, 0.9, and 1.2 ppm SO_2 for 1, 2, 3, and 4 hours on stomatal response of gray birch (*Betula populifolia* Marsh.), yellow birch (*B. lutea* Michx. f.), and European white birch (*B. pendula* Roth.). The stomatal conductance rate of yellow birch and European white birch increased after exposure to 0.3 ppm SO_2 for 1 and 2 hours, but decreased in response to the higher doses. In gray birch, stomatal conductances increased only after exposure to 0.6 ppm SO_2 for 1 and 3 hours, and decreased in response to all other doses. Similar results were obtained by Noland and Kozlowski (1979) with American elm (*Ulmus americana* L.) and by Suwannapinunt and Kozlowski (1980) with silver maple and black locust (*Robinia pseudoacacia* L.). Fumigation of silver maple and black locust seedlings with 0.75 ppm SO_2 for 2 to 16 hours increased transpirational water loss, but transpiration declined as the duration of fumigation increased.

The initial effect of SO_2 on stomatal opening may be related to reduced turgor in the subsidiary cells (Suwannapinunt and Kozlowski 1980; Heath 1980). A rapid preferential absorption of SO_2 by the subsidiary cells followed by changes in the permeability of membranes and decreases in cell turgor may account for wider stomatal apertures and increases in transpiration (Squire and Mansfield 1972;

Biscoe et al. 1973). As the SO_2 concentration or duration of fumigation is increased, the induction of stomatal opening subsides and the stomata eventually close (Noland and Kozlowski 1979). Stomatal closure at high doses of SO_2 may be associated with accumulation of CO_2 in the substomatal cavities following SO_2 inhibition of photosynthesis (Sij and Swanson 1974). Changes in the permeability of guard cell membranes also may be involved (Puckett et al. 1977).

Little information is available on the impact of oxidants on stomata of woody plants. Coyne and Bingham (1982) compared photosynthesis of slightly, moderately, and severely injured ponderosa pine in mature stands naturally exposed to oxidant fumigation. They found that the ratio of stomatal CO_2 resistance to the total resistance decreased with increasing oxidant injury and needle age. This observation suggests that the loss of photosynthetic capacity was related primarily to the loss of chloroplast function rather than to increased resistance of CO_2 diffusion through the stomata.

Particulates and heavy metals may influence plant photosynthesis by affecting the stomata in several ways. One way is by physically plugging the stomata Williams et al. (1971) examined leaves of oak (*Quercus petraea* (Malluschka) Leibl.) downwind from a fuel plant. He observed that the surface deposits resulted in a significant increase in the number of stomata with particulate matter in their pores, and suggested that this would result in large concentrations of sulfur within the leaves and increased water loss. Czaja (1966) showed that stomata of conifers may be plugged by dust, preventing the normal exchange of gas.

A second way that particulates may inhibit stomatal activity was proposed by Czaja (1962). In the presence of cement dust, the hydration process of crust formation releases calcium hydroxide. This alkaline solution may penetrate the stomata and injure the cells beneath. This process may be important in conifer species with exposed stomata. The alkaline solution also may saponify the protective cuticle on the leaves and needles and then migrate through the epidermal cells and injure the palisade and parenchyma tissue.

Heavy metals may influence stomata by inhibiting stomatal behavior. Lamoreaux and Chaney (1978) reported that the diffusive resistance of leaves generally increased with increasing cadmium concentration in excised leaves of silver maple. Cadmium is known to reduce transpiration in a variety of species by inhibiting stomatal opening (Bazzaz et al. 1974a, b; Carlson et al. 1975; Carlson and Bazzaz 1977).

Chlorophyll

The chlorophyll content of leaves fumigated with atmospheric pollutants has been measured in several studies. The data, however, are very conflicting.

Ricks and Williams (1975) reported a difference in the relative rate of degradation of chlorophyll a and chlorophyll b in oak leaves in naturally polluted areas before leaf fall. Chlorophyll a was degraded 4 times faster than chlorophyll b in the polluted site; in the control site, both chlorophylls degraded at about the same rate. Ricks and Williams (1975) concluded that the breakdown of chlorophyll a and b is a poor indicator of air pollution damage.

Mann et al. (1980) also studied the chlorophyll content of woody species in a natural environment. In studying selections of white pine that were sensitive or tolerant to air pollution, they observed no differences in photosynthesis between the two groups on a needle-weight basis, but they did find differences in the chlorophyll content. The chlorophyll content of new needles in the tolerant selection was approximately 15% higher than that in sensitive selections. The average chlorophyll content of current-year needles of the tolerant selection was 11% greater over the growing season; in 1-year-old needles the chlorophyll content of sensitive selections was 50% less than that of tolerant trees. Mann et al. (1980) suggested that the lower chlorophyll content may be due to the direct action of the pollutant on the photo-pigment, or may be a secondary result of nutrient deficiency from reduced carbohydrate for root growth.

Controlled fumigations have resulted in conflicting results. After 12 hours of fumigation with 2 ppm SO_2, Krawiarz et al. (1979) found that the content of chlorophyll a in poplar leaves (*Populus hybrida* 275) had increased 5 times while the content of chlorophyll b had increased 2 times. After 32 hours of fumigation, the leaves had visible injury and the chlorophyll content decreased. Suwpannapinunt and Kozlowski (1980) reported that treatment with 2 ppm SO_2 for 1 or 4 hours significantly reduced the chlorophyll content of young black locust seedlings, but had no effect on chlorophyll in leaves of American elm seedlings.

This problem was studied in detail by Malhotra (1977), who used lodgepole pine (*P. contorta* Dougl.) needles and aqueous sulfite solutions. Solutions representing 100 to 500 ppm SO_2 caused a sharp decrease in the total chlorophyll content, with chlorophyll a being more sensitive to SO_2 than chlorophyll b; SO_2 caused a conversion of chlorophyll a to phaeophytin a and chlorophyll b to chlorophyllide b. The process by which chlorophyll disintegrates may depend on the exchange of the central magnesium atom in the chlorophyll molecule. This reaction takes place readily in an acid medium. Malhotra, however, concluded that the exchange was due to the specific direct action of SO_2 and not a function of acidity. Ziegler (1975) stated that in any case the destruction of chlorophyll by SO_2 was too slow a process to account for the rapid decrease in photosynthesis. This suggestion is supported by Hallgren and Gezelius (1982). They concluded that the decrease in chlorophyll could be caused by the effect of SO_2 on synthesis of chlorophyll and not by chlorophyll degradation.

Chloroplast and Membrane Effects

Studies with the electron microscope have demonstrated that air pollutants can cause the breakdown of chloroplast and cell membranes. Malhotra (1976) studied the effect of SO_2 on the ultrastructure of lodgepole pine needles using aqueous solution representing 100 to 500 ppm SO_2. The SO_2 solutions caused swelling of the thylakoid discs and disintegration of the intrachloroplast membranes. The structural injury of chloroplasts was more pronounced in old tissue than in younger and more metabolically active tissue. Noble et al. (1980) examined tissue that had been injured by fumigation with O_3. The injured leaves showed a slight reduction in starch content and a reduction in the number of thylakoids per granum. Also, there was frequent blebbing of cytoplasmic membranes into the vacuole.

Respiration and Other Physiological Processes

In this paper, photosynthesis is reported as net photosynthesis without correction for dark or photorespiration. The reported values may be indirectly affected by the influence of air pollutants on these processes. Barnes (1972) reported that 0.15 ppm O_3 stimulated respiration in four young pine species treated for 5 to 18 weeks. Respiration was stimulated 27% in 4-month-old white pine seedlings fumigated for 5 weeks with 0.05 ppm O_3. Lorenc-Plucinska (1978b) reported that a fumigation of 1 ppm SO_2 6 hours a day for 3 days inhibited photorespiration in Scotch pine seedlings. Similar results were found with susceptible Scotch pine seedlings treated with O_3 (Lorenc-Plucinska 1979).

The photosynthetic process includes a large number of chemical and enzyme reactions (Bidwell 1974). Pollutants that interfere with any of these reactions, cause enzyme degradation, or interfere with enzyme synthesis could affect the total photosynthetic process. An important enzyme that may be affected by pollutants is ribulose biphosphate (RUBP) carboxylase. This enzyme adds CO_2 to ribulose. Hallgren and Gezelius (1982) found that photosynthesis decreased with an increase in SO_2 dose, and that this decrease was correlated with a similar decrease in RUBP carboxylase activity.

CONCLUSION

Most, if not all, of the atmospheric contaminants can influence photosynthesis. At moderate to high concentrations, the influence usually is harmful, causing a reduction in the photosynthetic rate. This reduction often is enhanced if two or more pollutants are present, but if the pollutants are removed before injury occurs photosynthetic rate may recover. The concentration component of pollutant dose appears more important than duration. The mechanism by which the pollutants affect plants is complex and involves many processes. It may be caused by an inhibition of the opening or closing of stomata aperture, destruction of the chlorophyll pigments, disruption of chloroplast ultrastructure, increasing respiration, or other physiological processes.

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TECHNICAL SESSION III
EFFECTS OF ACID RAIN ON FOREST VEGETATION

Recent Changes in the Growth of the Forest Trees in the Northeastern United States

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ABSTRACT

Increment cores from *Picea rubens* Sarg. in the montane boreal forests of New York, Vermont and New Hampshire show a clear and substantial reduction in growth which began in the early to mid-1960s and preceded a general decline of that species in the high-elevation forests of the Northeast. In the sandy soils of southern New Jersey, *Pinus rigida* Mill. and *Pinus echinata* Mill. show a very similar decline in increment size beginning in the late 1950s. The decreased growth effect is, in each case, widespread, substantial and sustained through to the present time, and suggests substantial physiological impairment. The timing of the shift to abnormally slow growth suggests that it is an after-effect of drought stress. Although there are many pathways by which pollutant stress (including acid deposition-induced stress) could contribute to stress in forests, there is currently no evidence which clearly links pollution stress to the observed changes in growth.

INTRODUCTION

There has been a great deal of research focused on the potential effects of acidic deposition on forest productivity. Much emphasis has been placed on a theoretical approach in trying to predict what the long-term consequences may be, and considerable emphasis has been placed on experimental work using simulated acid rain and measuring plant responses. To date, there are experimental results on aspects of germination, seedling establishment, growth, morphology and a variety of biochemical and physiological processes. Direct effects have been sought, as have effects on trees resulting from changes in soil chemical properties. We now have a substantial amount of information which allows an understanding of the potential effects of acidic deposition. There is, however, a lack of understanding of what acid deposition is actually doing in forests. It has come to light recently that there have been widespread, substantial and sustained decreases in the growth of certain forest species which began during the past 20 years. Affected species identified to date are red spruce (*Picea rubens*), pitch pine (*Pinus rigida*) and shortleaf pine (*Pinus echinata*). The reduction in growth of red spruce preceded widespread mortality and decline of that species in New England. One obvious question is, of course, is acidic deposition related to the changes in growth?

Linking acidic deposition to changes in growth has proved to be a difficult undertaking. Measurements of the chemical composition of affected trees, correlations between acid deposition rates and precipitation pH have not provided much evidence strengthening the contention that acid deposition is responsible for recent changes in the forest. Although the theoretical and experimental results have defined pathways by which acid deposition may be acting, it is difficult to extrapolate the results to field situations. The main limiting factors are as follows:

1. The experimental work has generally focused on a single stress (acid deposition) and measured, at most, a few responses in forest species. In the field, trees are subject to numerous stresses which may act synergistically to cause effects not predicted by the experimental work.

2. Tissue chemistry studies have shown differences among affected and unaffected trees, but it is difficult to determine if the differences are a cause or an effect of stress.

3. Essentially no data exist on the physiological changes which have accompanied the observed growth reductions or mortality.

4. Few baseline data from the period before 1960 exist against which recent data on soil and vegetation characteristics can be compared in order to evaluate long-term changes.

This paper summarizes the extent and nature of growth changes in pines and spruce, summarizes the evidence regarding the possible involvement of acid deposition, and presents our ideas on needed research.

NEW JERSEY PINELANDS STUDY

The Pinelands region of southern New Jersey encompasses approximately 2500 km^2, and is characterized by nutrient-poor, acid sandy soils. The growth rate decline in pitch and shortleaf pines was described by Johnson et al. (1981) and is prominent across the region on Quartzipsamments and Hapludults soils which have a pH in the range 3.5-4.5 and a very low CEC (0-4 meq 100 g^{-1}). There is relatively little neutralization of atmospheric acids in the soil by ion exchange or mineral weathering (Johnson 1979; Turner 1983). Long-term sampling indicates that headwater streams in the Pine Barrens have become increasingly more acid since the early 1960s, with SO_4^{2-} being the main acid anion balancing H^+. Johnson (1979) concluded that the most reasonable explanation was acidification of the precipitation coupled with a lack of buffering by the old, highly weathered soils.

About one-third of the pines (*Pinus rigida* and *Pinus echinata*) show a readily apparent, abnormal decline in increment size. Abnormally narrow rings first appeared between 1956 and 1965, regardless of age or species. The first year of diminished growth varied from tree to tree, but 1957 was an important year for the initiation of the event (Figures 1, 2). In comparing old (80-100 yr) and young (40-60 yr) trees growing at six sites, Johnson et al. (1981) showed that the trees grew at the same rates initially, but after 20 years of growth, the younger class grew significantly more slowly (Figure 3). The period of reduced growth was in the 1955-1979 interval. Comparison of patterns of stream pH and growth rates showed a marked similarity during the 1963-1979 period (Figure 4). Multiple regression and multivariate analyses, using approximately 20 potential growth-controlling factors, indicated that stream pH (shown to be a reasonable proxy for precipitation pH (Johnson et al. 1981)), drought, winter temperature, winter moisture, spring and summer insolation were significant variables related to growth after 1955, but not before 1955. The change in factors to which tree growth responded and the decrease in increment size suggest the emergence or strengthening of some stress or stresses during the mid-1950s. The delayed response, and the prolonged nature of the abnormally narrow annual increments, are unexplained at present, but likely represent important physiological changes in the trees induced by environmental stress. As elaborated by Johnson et al. (1981), ozone and SO_2 do not appear to be involved in the shift to diminished growth, but the evidence is not conclusive in that regard.

SPRUCE GROWTH AND SPRUCE DECLINE

Stress-related diseases, the diebacks and declines, have been responsible for extensive hardwood mortality during the past few decades (Manion 1981). Recent observations of red spruce in the high-elevation forests of New York and New England have indicated substantial and widespread mortality under circumstances which bear the characteristics of stress-related disease. Such diseases are characterized by predisposing, triggering and contributing stresses which result in gradual weakening, loss of foliage (dieback), invasion of secondary pathogens and, in many cases, mortality.

Dieback of Norway spruce (*Picea abies*), silver fir (*Abies alba*) and beech (*Fagus sylvatica*) has been reported in several areas of West Germany (Ulrich 1982), and several similarities between the North American and European cases suggest that the diseases may have similar origins. Because the declining forests are in areas which receive high rates of acid deposition, and because there are no obvious causes to which the mortality can be attributed, considerable attention has been given to the possibility that acid deposition contributed to the observed dieback.

Nature of the Declining Stands

Red spruce is a long-lived (300+ yr), shade-tolerant species, which is a major component of the mid- to high-elevation forests of the Appalachian Mountains. Most research to date has centred on the montane boreal forests, rather than on the economically important low-elevation stands which cover large areas of northern Vermont, northern New Hampshire, Maine and Canada. Little has been reported on the status of spruce dieback in the latter set of forests. The northern montane boreal forests are characterized by red spruce, balsam fir (*Abies balsamea*) and white birch (*Betula papyrifera* var. *cordifolia*) in the canopy. In the northern Appalachians, the lower slopes are occupied by a hardwood forest dominated by sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*). Between the boreal and northern hardwood forests is a narrow transition zone where neither set of species dominates. Red spruce is a major component of the transition forest, and a minor component of the northern hardwood forest.

The soils which support declining red spruce vary considerably in morphology and chemical characteristics. In the northern Appalachians, at elevations above ca. 750 m, the soils are typically very acid (pH 3.5-4.5) and are low-base status Orthods, Humods or Folists. Below 750 m, Orthods or less acid (pH 4.5-5.5) Ochrepts dominate. In the southern Appalachians, the dominant high-elevation soils are Ochrepts, Umbrepts, Udults or Spodosols.

Although the mountain summits are remote from large point sources of atmospherically borne pollutants, they receive extraordinarily high rates of acid deposition and heavy metal deposition, due to high precipitation rates and the interception of very acid cloud moisture by the coniferous vegetation. From the data of Lovett et al. (1982) it appears that the mid- to upper-slope forests receive 2-3 Keq H^+ ha^{-1} yr^{-1}, which is approximately three to four times the deposition rate measured at low elevations in the Northeast. In addition to the high rates of acid deposition, the montane boreal forests are above cloud-base for considerable portions of the year. Siccama (1974) estimated that in the northern Green Mountains, the spruce-fir forests are above cloud-base for 800-2000 hours per year, depending on elevation. As cloud moisture is particularly acid (averaging ca. pH 3.5 during the growing season (Siccama 1974)), the potential for direct effects on vegetation appears to be high. Friedland et al. (1984) and Johnson et al. (1982) have shown that Pb concentrations in the organic horizons of Green Mountain forest soils have increased dramatically over the past two decades, and that current Pb levels are in the range observed in polluted urban soils. Several lines of reasoning described by those authors suggest that most of the accumulating Pb is derived from the atmosphere, and that current Pb levels in the boreal forest soils are about 10 times greater than pre-settlement levels. Other metals, including Cu, Zn, Ni and Cd, are also deposited in remote regions of New England (Friedland et al. 1984a, 1984b). Thus the montane boreal forests which are generally viewed as pristine environments are actually highly polluted ecosystems as a result of long-distance atmospheric transport. At the present time, we do not know what role, if any, the accumulating heavy metals may play in the spruce decline, but we speculate that they, like acid deposition, *could* play a role.

Extent of Red Spruce Decline

In 1982, quantitative surveys were conducted to assess mortality and dieback (needle loss) in 32 stands of the northern and southern Appalachians. Details of sampling designs and analytical procedures are given elsewhere (Zanes 1982). Tissue chemistry and quantitative surveys of stand composition were carried out in 1981 and 1982 as detailed elsewhere (Zanes 1982; Siccama et al. 1982; Holway and Scott n.d.; Scott et al. n.d.; Lord 1982).

Table 1 summarizes the changes in basal area observed at Whiteface Mt., NY, in the Green Mountains of Vermont, and at Hubbard Brook, NH, over the past 20 years. There have been substantial losses of spruce in a wide variety of forests which cover a broad area. Mortality has occurred on a large scale and rather evenly across small and large size classes. At some sites, fir and white birch show reductions in basal area, but generally to a lesser degree. Figure 5 shows that the mortality we observed is largely confined to the area north of Pennsylvania. Recent reports (Bruck, pers. commun.) suggest that spruce are dead or dying on the summit of Mt. Mitchell, NC (above 1920 m). Considerable spruce and fir mortality has been noted in Maine and attributed to spruce budworm infestation. Because of the known problems associated with that insect pest, the survey was confined to areas known to be free of budworm infestation.

Figure 1. Example of a pitch pine core showing slow growth rates in the past 20 years.

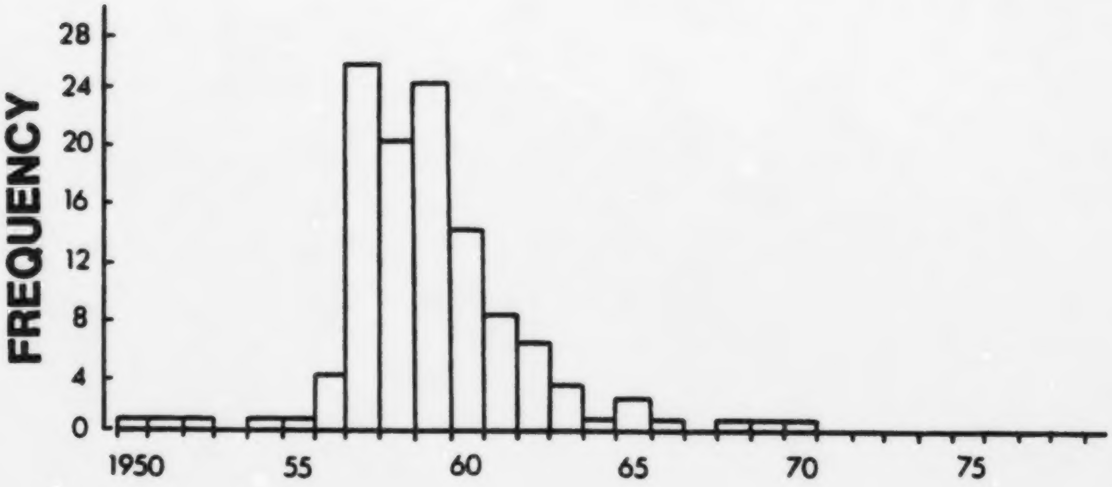

Figure 2. Frequency of appearance of the first short annual ring in New Jersey pitch and shortleaf pine. After Johnson and Siccama, 1983.

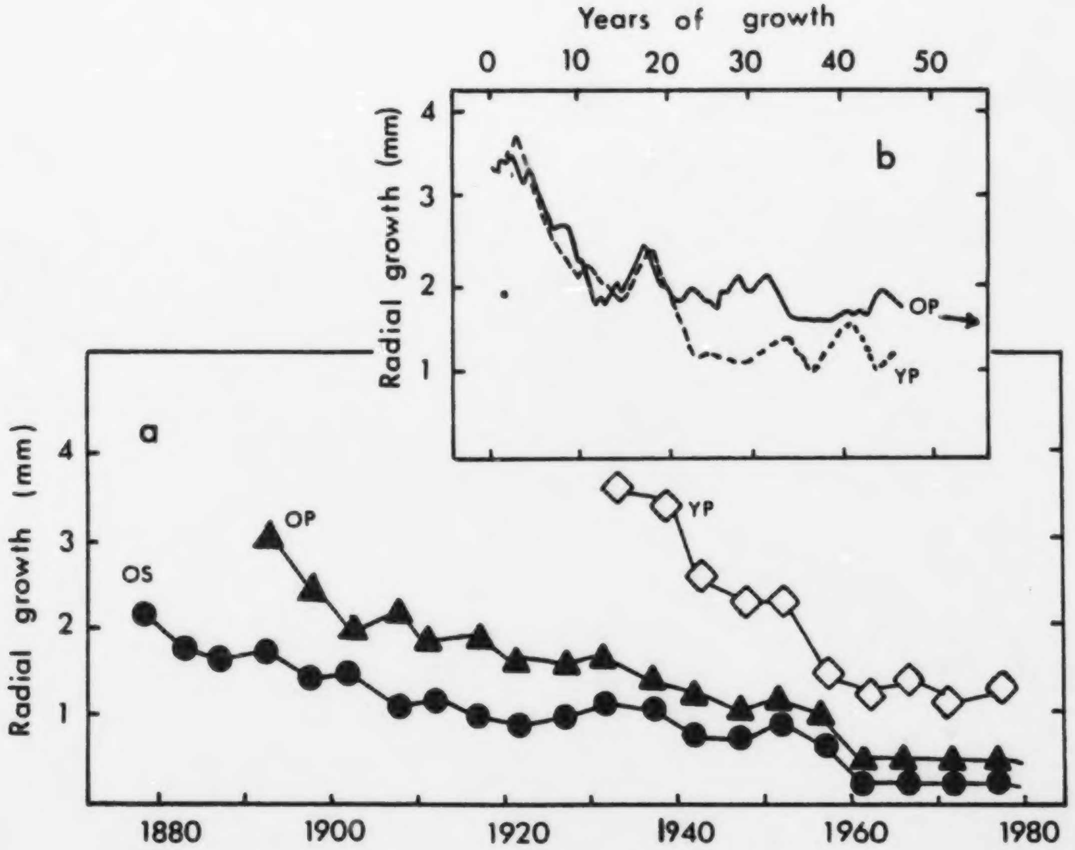

Figure 3. Radial growth vs time. OS (Old Shortleaf Pine) is 90-110 year age class (15 trees, 4 sites); OP (Old Native Pitch Pine), 80-100 year (30 trees, 6 sites); YP (Young Native Pitch Pine), 40-60 year (32 trees from the same sites where OP cores were collected). a represents 5-year averages; b shows each year's growth as a function of age. Symbols represent mean ± one SE. After Johnson et al., 1981.

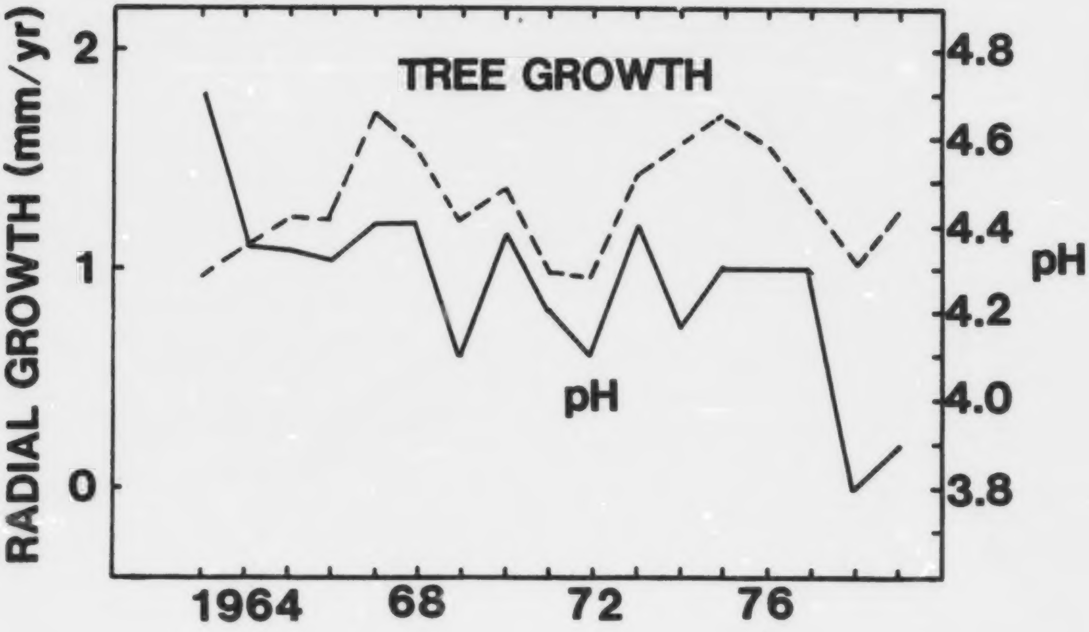

Figure 4. Yearly average stream pH at McDonalds Branch, New Jersey Pine Barrens, and mean yearly increment size of young native pitch pine (n = 32 trees, 40 - 60 year age class). After Johnson et al., 1981.

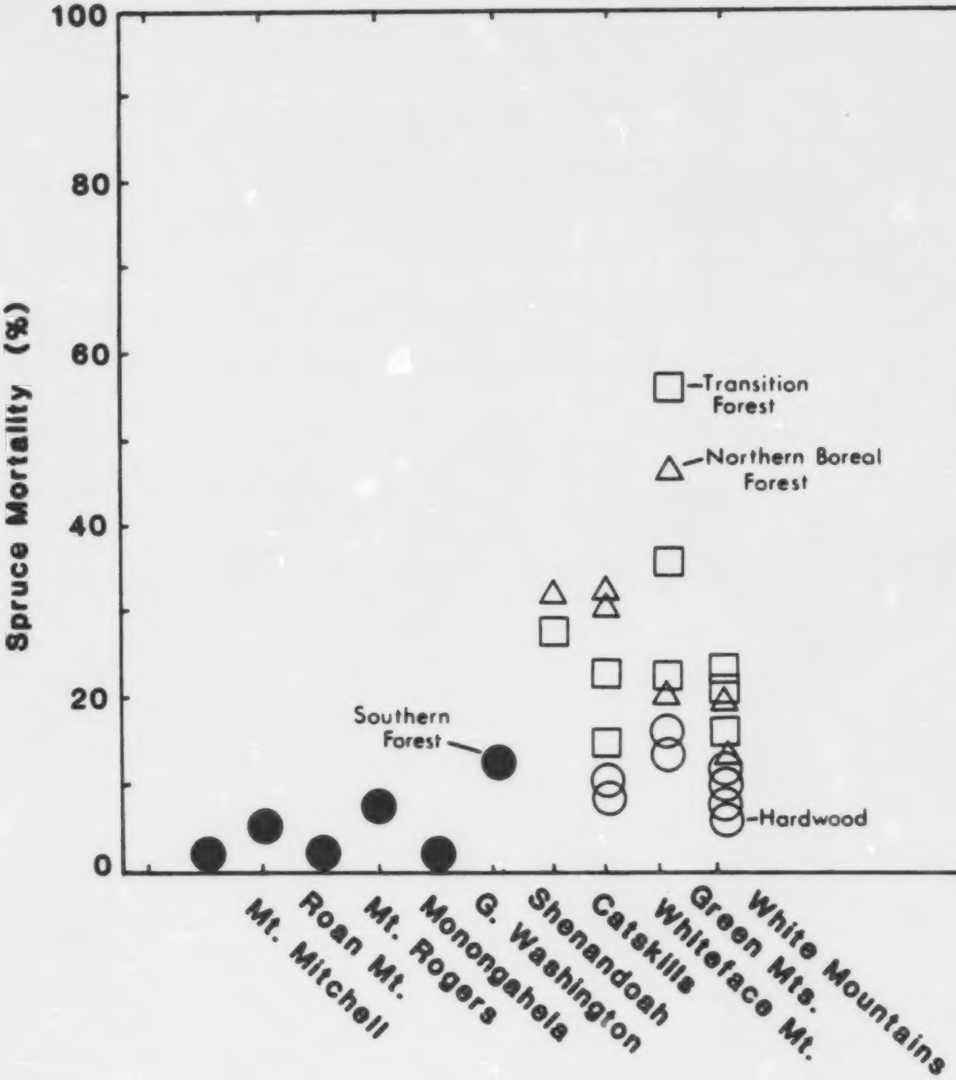

Figure 5. Percentage of dead spruce in northern and southern sampling sites. Methods are given by Zanes, 1982. After Johnson and Siccama, 1983.

Table 1. Changes in stand composition in the Green Mountains, White Mountains and Whiteface Mountain during the past two decades. Data shown are change from the initial value[1]

				Red spruce dbh (cm)[2]			Balsam fir dbh (cm)			White birch dbh (cm)		
Site	Stand type	No. plots	Interval	>10	2-10	<2	>10	2-10	<2	>10	2-10	<2
Camels Hump (VT)	boreal	25	1965-79	-44	-42	-32	-12	+19		-22	+433	
	transition	20	1965-79	-40	-84	-71	+17	-32		+263	-28	
	hardwoods	40	1965-79	-42	-80	-50				+306		
Jay Peak, Mt. Abraham, Bolton Mt. (VT) (pooled)	boreal	32	1965-79	+2	-69		-10	+2		-7	-46	
	transition	24		-87	-90		-24	-74		-73	+33	
Hubbard Brook (NH)	hardwoods	208	1965-82	+29	-83		+60	-73		+176	-65	
Whiteface Mt. (NY)	boreal	21	1964, 1966-82	-72	-16	-79	-34	+52	+8	-33	+239	+6
	transition and hardwoods	12	1964, 1966-82	-43		+12			+42			+252

[1] After Johnson and Siccama (1983).

[2] Changes in basal area are for the two larger size classes. Changes in frequency or density are given for the <2 cm dbh class.

THE TREE RING RECORD

Increment cores were obtained from approximately 700 spruce in the northern and southern Appalachians. These show that at the northern sites there was a dramatic decrease in increment size which began in the early- to mid-1960s and continued to the present. Examination of individual cores showed that in 40% of the trees cored at the northern sites, there was a rather abrupt shift to abnormally narrow increments (Figure 6). This is essentially the same pattern as observed in the southern New Jersey pines illustrated in Figure 1. The appearance of the first abnormally narrow increment is distributed in time as shown in Figure 7. In spruce and in pines, this effect is widespread, substantial and sustained, and appears to have important implications. Although the appearance of the tree cores is the same across the array of affected species, detailed information on differences which may have occurred in cell size and wood density are currently lacking. It is not certain that the trees are responding to the same changes in physiology. As stated in other publications, we have reviewed the existing evidence regarding possible causes for the changes in growth and for the spruce mortality (Johnson et al. 1981; Johnson 1983, 1984). Major episodes of mortality in forests have been related to a wide variety of causes, both anthropogenic and natural. Acid deposition is but one of many stress factors acting on forests. As research progresses, it will be necessary to give equal treatment to several potential factors about which we currently have little quantitative information, such as ozone, SO_2, long-term climatic change, heavy metals and the effects of drought.

One factor which appears to be common between the southern New Jersey and montane boreal forest cases is that the decline in growth follows a period of drought. The early- and mid-1960s were a noted period of drought in the Northeast. Figure 8 shows the minimum Palmer Drought index which occurred during the growing season in Vermont over the past 85 years. Several other indicators which may be more appropriate to moisture stress at high elevations have been examined. These include precipitation from summit weather stations from Mount Mansfield, VT, and Mt. Washington, NH, and modelled soil moisture conditions in New Hampshire (Federer 1980). Those data confirm that high- and low-elevation stands of the northern Appalachians experienced several relatively dry growing seasons during the late 1950s through to the early 1960s. In the case of the pines of southern New Jersey, the relationship of the loss of vigor to drought is clear. Figure 9 shows that 1957 had the driest growing season on record, and that 1954 and 1955 were also very dry. Although delayed response to drought of two or three years is well-known (Kozlowski 1979), we do not suspect that drought alone can account for the very long delay in some trees, nor do we know whether drought alone is responsible for the prolonged effect. We speculate that drought stress may have combined with pollution stress to produce the observed effect. In our experience, such a substantial and prolonged growth response has not been reported before.

POSSIBLE ACID DEPOSITION EFFECTS

Whether or not acid deposition is involved in the two cases reported here is not known at present because there is no clear indication which mechanisms might be involved. We have tested one hypothesis regarding Al toxicity to root tissue in a field study (Johnson and Siccama 1983), and we propose another—that acid deposition could enhance drought stress.

From studies in the Solling forest of West Germany which have spanned a decade and a half, Ulrich (1982) and Ulrich et al. (1980) have suggested that increased acid deposition has caused or contributed to changes in H^+ generation and consumption in forest soils. This has led to soil acidification and mobilization of Al, which in turn have caused fine, root mortality and ultimately dieback of Norway spruce, silver fir- and beech. The scenario of Ulrich et al. is based on careful documentation of changes in soil chemistry, a nearly parallel decrease in fine-root biomass and an increase in soil-solution Al concentrations, and nutrient-solution studies which showed that the ratio of uncomplexed Ca:Al found in the soil solution was in the range sufficient to cause abnormal root development. Although those findings suggest the possibility of acid-deposition-induced Al toxicity, other research suggests different mechanisms. Bauch (1983) studied declining spruce and fir in Germany and observed that the roots were calcium deficient relative to those of healthy trees, and that healthy and declining trees had similar Al concentrations. Rehfuess (1981) observed declining fir on calcareous soils, a finding which precludes Al toxicity or Ca deficiency in those cases. Rehfuess showed that the parallel decrease in fine-root biomass and increase in soil-solution Al noted by Ulrich were not synchronized. Marked decreases in root biomass preceded the increase in soil-solution Al. Rehfuess contended that seasonal changes in fine-root biomass are normal phenomena, and he proposed that a series of dry summers could have promoted the dieback of the European conifers.

The application of Ulrich's hypothesis to red spruce decline in North America is not supported by tissue chemistry studies carried out in declining and healthy stands of spruce in Vermont and New Hampshire. Studies reported by Johnson and Siccama (1983) and by Lord (1982) indicated that declining spruce could have low Al concentrations (less than 500 $\mu g\ g^{-1}$ dry wt.) and that healthy spruce could have high (greater than 2000 ppm) Al levels. Similar patterns were observed with Al:Ca ratios. At Camels Hump, VT, spruce are declining at low elevations where soil pH is in the range 4.5-5.4 and available Ca is approximately 5 meq 100 g^{-1} (Siccama 1974), as well as at high elevations where soils are essentially organic mats (Borofofists and Cryofolists) overlying bedrock or felsenmeer (literally "sea of rocks"). The organic soils have pH values ranging from 3.3 to 3.7 and exchangeable Ca of less than 1 meq 100 g^{-1}. The Al content and the Al:Ca ratio in fine-root tissue both decrease substantially with increasing elevation (Johnson and Siccama 1983). Likewise, there is a significant trend of decreasing Al in spruce foliage with increasing elevation, indicating reduced availability of Al in the organic soils. Since mortality is directly correlated with elevation (Figure 10), it does not appear likely that Ca or Al imbalances are primarily responsible for the spruce decline.

It is possible that prolonged exposure of foliage to acid cloud moisture could contribute to drought stress. Shriner (1974) observed that artificial acid rain at pH 3.2 was associated with accelerated erosion of or decreased production of leaf surface waxes, and the data of Fowler et al. (1980) suggest that the resulting potential for water loss through the leaf surfaces could be an important factor when moisture is limited. Owing to the prolonged exposure to very acid cloud moisture, foliar effects of this type are plausible, as are other potentially important foliar effects.

Several investigations show that with acid simulants in the range of pH 3-4, changes in the soil solution chemistry occur, with elevated levels of Al being prominent (Abrahamssen Stuanes 1980; Cronan and Schofield 1979). It is possible that changes in the soil solution chemistry could inhibit water uptake by plants. Indeed, such an effect has been documented in the case of Al (Klein 1983). Thus, in our view changes in the soil solution which inhibit water uptake or transport could have contributed to the marked changes in growth: the effects of the dry summers could be exacerbated by acid deposition.

Johnson et al. (1982) reviewed the possible effects which acid deposition could have on forest nutrient status, and pointed out a variety of ways in which acid deposition could alter cycling rates and pool sizes of nitrogen, sulfur and the essential nutrient cations Ca, Mg and K. Unfortunately, there are very few data applicable to the spruce and pine forests which allow confident assessment of whether or not such changes have occurred during the "acid rain era". Plant tissue analyses reported by Lord (1982) for declining and healthy spruce do not differ substantially from values reported for red spruce sampled in Maine and in Canada, except perhaps for low levels of root Ca observed in declining stands in Vermont, a finding which merits further investigation, particularly in light of similar findings in Germany (Bauch 1983). However, as spruce are declining in soils with abundant Ca, as well as in soils with extremely low levels, it does not seem likely to us that nutrient deficiencies are the main cause of spruce decline. Current research in the Pinelands may yield information on the nutrient status of the pines, but no evidence is available at present.

Figure 6. Example of a spruce tree core showing a rapid shift to abnormally narrow increments with no signs of recovery.

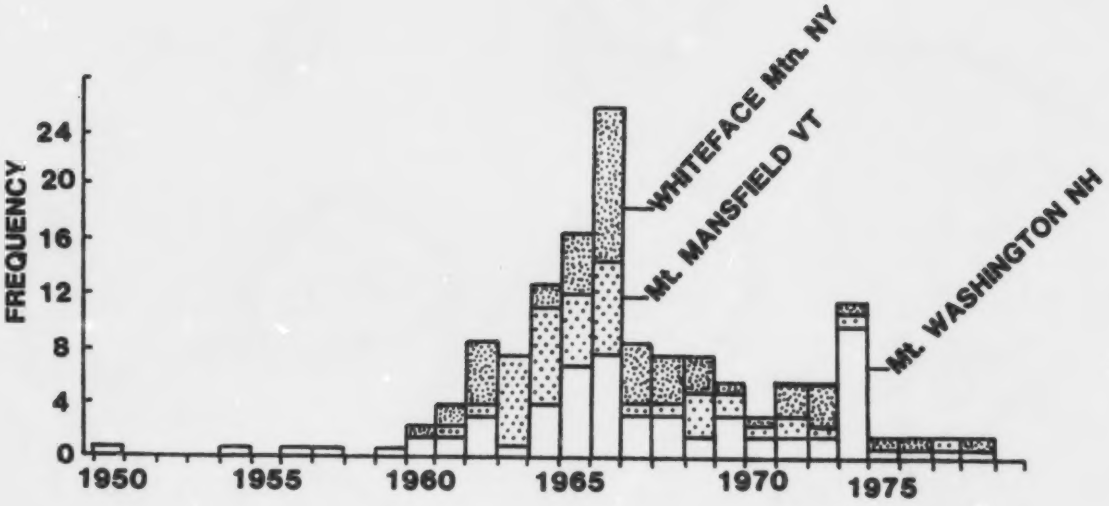

Figure 7. Frequency of appearance of the first short annual increment in 148 spruce trees that showed a rapid shift from normal growth to slow growth. A total of 345 trees were sampled. After Johnson, 1983.

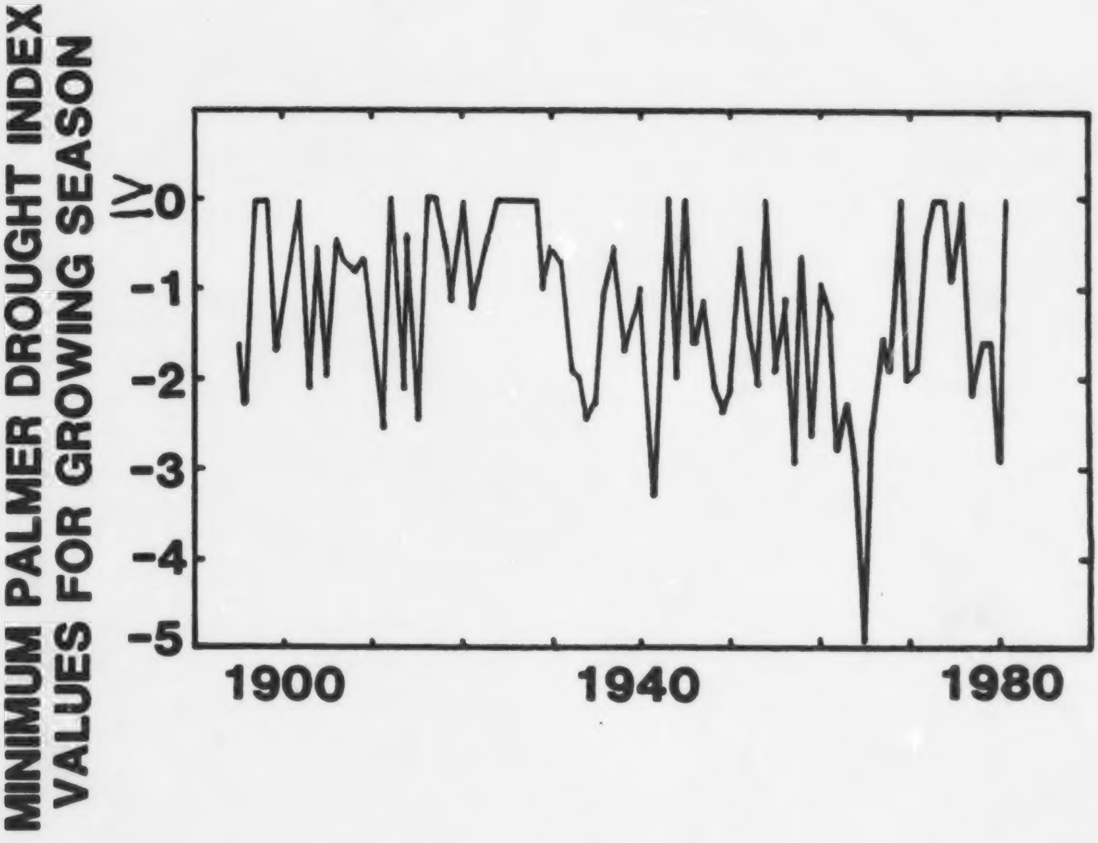

Figure 8. Palmer Drought Index values for Vermont from 1895 to 1981. After Johnson and Siccama, 1983.

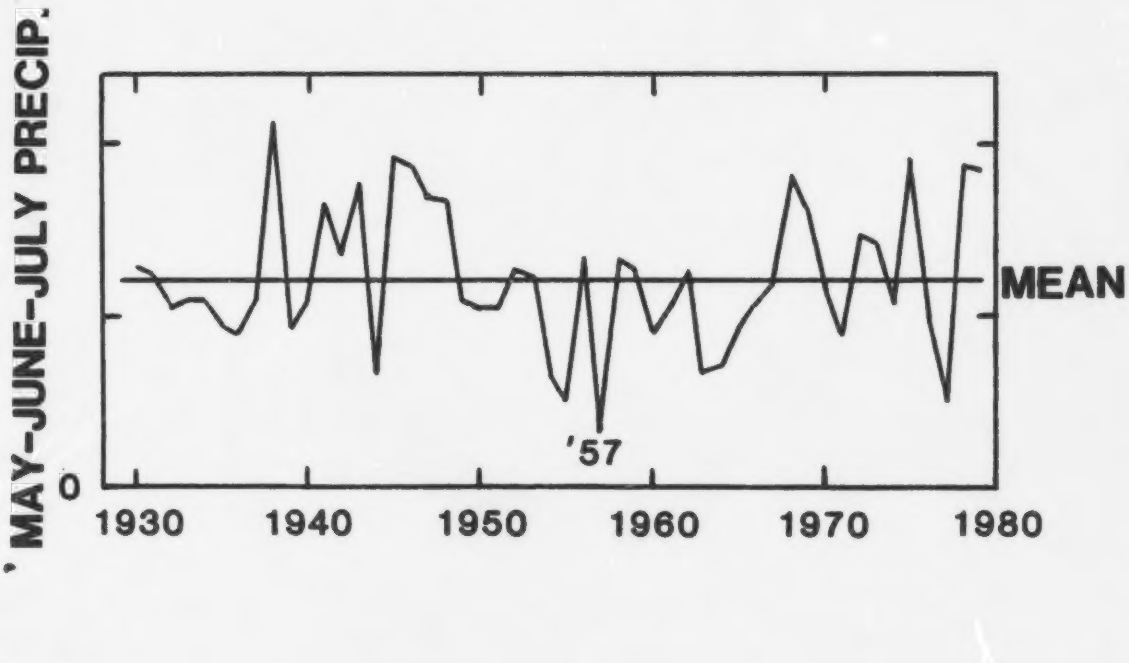

Figure 9. Precipitation during the growing season, Pemberton, NJ. After Johnson and Siccama, 1983.

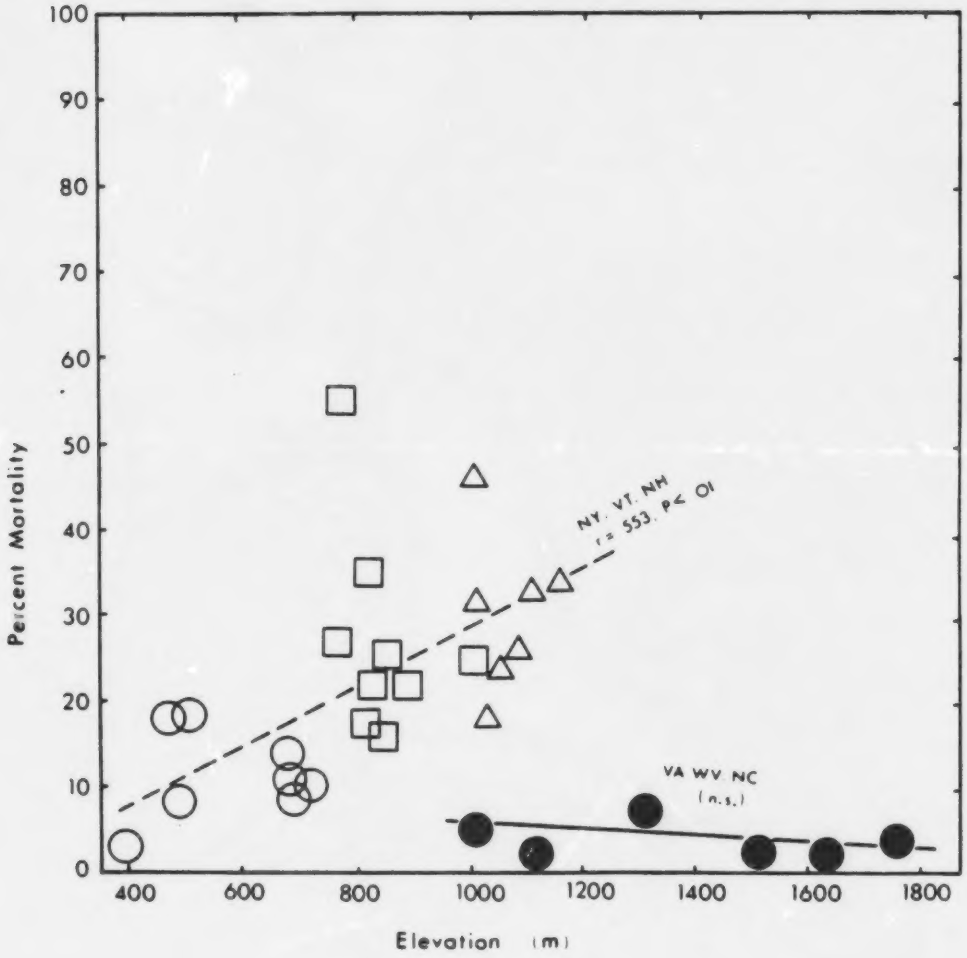

Figure 10. Percent mortality correlated with elevation from the northern sites. Symbols are the same as in Fig. 5. $r = 0.553$, $p < 0.01$. Methods are given by Zanes, 1982. After Johnson and Siccama, 1983.

SUMMARY

Very clear evidence of changes in tree growth has emerged from tree core studies. These changes affect a variety of species, are widespread, substantial and sustained, and are occurring in widely different ecosystems which have very marked differences in soil characteristics. It is equally clear that the affected areas are subject to heavy loadings of acid, trace metals, and perhaps other pollutants (such as organic compounds) which have not yet been studied carefully. We believe that the evidence suggests that drought or a series of dry summers are involved in creating stress, which results in important and lasting physiological changes manifested in diameter growth. It is not clear whether or not additional pollution stress has contributed, and further work must be designed to test mechanisms by which acid deposition or other pollutants can contribute. Investigation of the possibility of Al toxicity to fine roots is not conclusive, but does not support that mechanism in the case of red spruce in the New England mountains. Owing to the association of vigor loss with drought periods, we suggest that experiments designed to determine interactions between acid deposition and drought stress would be of interest.

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DISCUSSION

Question: Several were raised and were grouped into four themes: (1), the role of aluminum in spruce decline. (2), the response of spruce to prior drought periods, (3), the reproduction of spruce in drought-stressed stands, and (4), the tree-ring evidence for boreal species, mainly balsam fir.

Answer: First, what we found was a very distinct trend of increasing calcium to aluminum ratio in the fine roots. It is also true in the foliage in these stands. You will recall that there was an increase in mortality in spruce with increasing elevation. We know that from our survey of live and dead spruces and also from some quantitative stand sampling that was done in the 1960s and 1980s. So mortality gets worse as one goes higher on the mountains, but the calcium to aluminum ratio in the fine roots increases as one goes higher, and the aluminum concentration drops quite dramatically as one goes higher. Our interpretation of this is that the increasing organic matter content of the soils, as one goes higher, binds the aluminum more effectively, so that aluminum is not as available to the trees at higher elevation. One interpretation of this is that it is negative evidence for the involvement of aluminum toxicity to roots.

Secondly, with respect to earlier drought episodes, the last very dry period or one that was as dry as in the 1960s occurred around 1870. In 1901 a Forest Service entomologist was studying the eastern spruce beetle he had just identified as a new species. He looked through the literature which was largely anecdotal, but nonetheless produced by foresters of the time, to find out if there had been areas of drying and dead spruce in the 19th century. In the time period around 1870-1880 there are several reports from New England and also from Canada which suggest that there were declining spruce. I think the relationship between these large patches of dying spruce and the drought or dry summers that occurred around 1870 could be a causal relationship. Some might suggest that this evidence suggests spruce decline could be initiated by drought alone and need not be exacerbated by pollution stress.

Thirdly, as far as reproduction is concerned, from our surveys on Whiteface, Camels Hump and four other mountains, it is quite clear that spruce reproduction is down very dramatically, about 80%, and for one site -- which is Whiteface Mountain -- there is a decline in sapling or pole-size spruce, a slight increase in fir reproduction and a dramatic increase in the increment or the basal area change in fir and white birch. This suggests that some of these other species are coming into the forests where the spruce have died. Many of the stands that we have sampled show dead spruce in the canopy, with the regrowth of fir and birch coming in reasonably well. That appears to be good news as far as the continuation and health of the forest are concerned.

Fourthly, there may also be some bad news. We have begun to study intensively balsam fir, and we have looked at tree rings to tell us about height growth and diameter growth rates of fir. For Whiteface Mountain, the results suggested to us that we should look further. For trees that are at least 40 years old, i.e., those that started growing before 1950, at 10 years they were a little bit greater than a metre in height and they were about 2 cm in diameter at ground level. Trees that started growing after 1950 were considerably smaller, approximately 40 cm in height on average, and the diameter at 10 years was reduced by about a factor of three. We consider this to be preliminary evidence. We did this at two stands. We are doing it at 11 additional stands to try to get a better indication of how fir may be responding in the last two or three decades.

Sensitivity of Forest Plant Reproduction to Acid Rain

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ABSTRACT

The relevance of long range transported air pollutants to, and their effect on, reproductive processes of forest and native flora are reviewed and discussed. Included are some effects of ozone and sulfur dioxide as they relate to acid deposition or to combined effects with acidic deposition. In vitro and in vivo experiments that investigate the effects on pollen of acidic and trace element components of polluted rain are described. The in vitro pollen sensitivity to pH was related to canopy strata and plant taxon together with, in one instance, the soil type of the population from which it was collected. Most pollen assayed revealed that its threshold of response to pH is exceeded by the pH recorded for daily rain samples collected at one rural site in southern Ontario. The in vitro effects on pollen of cadmium and aluminum in combination with pH are discussed in relation to cation stimulation of pollen and to synergistic interaction with pH respectively. In vivo inhibition of pollen function by field simulations of acid rain on *Oenothera parviflora* is compared to similar inhibition by SO_2 fumigations, which have reduced seed set in some species. Given some evidence for correlations between tolerances of the pollen and their sporophytes, the possible effects of direct environmental selection of pollen genotypes on the stigmatic surface by air pollution are discussed with reference to fitness of future generations.

INTRODUCTION

In recent years, the significance of flowering and seed production in forest trees has gone beyond their natural role in reproduction and regeneration and lies more in the provision of seeds for production of genetically improved planting stocks (Chung 1981). Any impact of acidic precipitation on the quality and quantity of these stocks would have far-reaching consequences for future forest productivity.

Pollen development and activity are known to be among the more sensitive botanical indicators of atmospheric pollution (Feder 1968; Stanley and Linskens 1974; Feder 1981). Atmospheric pollutants may directly affect vulnerable reproductive processes at the time of pollination, either by directly reducing pollen viability and pollen tube growth or by affecting the chemical environment of the stigmatic surface, which may reduce stigma receptivity and change pollen stigma interactions.

Studies on conifers located at different distances from urban and industrial areas have shown marked reductions in cone dimensions, seed weight and viability, together with reduced pollen viability (Pelz 1963; Podzorov 1965; Mrkva 1969; Antipov 1970). Furthermore, these effects may occur at pollution levels lower than required for foliar injury (Houston and Dochinger 1977).

Ozone is a widespread atmospheric contaminant and, at low concentrations, has inhibiting effects on pollen germination and pollen tube growth in tobacco and corn (Feder 1968; Mumford et al. 1972). Correlations between pollen sensitivity and varietal foliar sensitivity to ozone in tobacco, petunia and tomato have been demonstrated by Feder and Sullivan (1969) and Feder (1981). However, Benoit et al. (1983) found no such correlation between foliar and pollen sensitivity in eastern white pine, but did find that moist pollen was more sensitive to O_3 than dry pollen.

The inhibitory effects of sulfur dioxide on pollen viability have been known since the pioneering work of Sabachnikoff (1912). Dopp (1931) assayed the SO_2 sensitivities of pollen of many species in different humidities and clearly indicated the increased toxicity of SO_2 under wet or high relative humidities (RH).

The increased acidity of SO_2 fumigations under wet or high RH was taken for granted by Dopp (1931), who suggested that the increased in vitro effect of the fumigations over in vivo effects was due to the extra buffering of the stigmatic surface. The acidity of sulfur dioxide solutions is due to the equilibrium:

$$SO_2 \bullet xH_2O \rightleftharpoons HSO_3\,(aq.) + H_3O^+ + (x\text{-}2)H_2O$$

(Powell and Timms 1974). The role of increased acidity in the pollen toxicity of SO_2 fumigation under high RH is not well documented. Karnosky and Stairs (1974), however, reported that the pH of an agar/sucrose gel pollen culture medium decreased from pH 7.0 to pH 5.0 after a 4-h fumigation with 1.4 ppm SO_2. It was also found that the depression in pH alone was sufficient to severely inhibit pollen germination and tube growth of the *Populus deltoides* marsh pollen tested. The H^+ ions present in such assays are therefore implicated as an important component in SO_2 pollen toxicity. This view was also supported more recently by Murdy (1979), and by DuBay and Murdy (1983a,b).

A growing list of species has been investigated for in vitro effects of SO_2 on pollen under high RH, as shown in Table 1. Murdy (1979), using in vivo SO_2 fumigations of different populations of *Lepidium virginicum* L. under conditions of high RH (>90%), was able to increase fruit sterility. Furthermore, the degree of sterility was related to the ambient air concentration in the populations' place of origin, which indicated the possible evolution of SO_2 tolerance of the reproductive system in SO_2-polluted populations.

DuBay and Murdy (1983a), however, were unable to increase sterility in *L. virginicum* under SO_2 fumigation, even though a 50% reduction in in vivo pollen germination was achieved. This may have been due to the selection of plants with good background self-fertility.

Table 1. Some in vitro studies of SO_2 effects on pollen activity under high relative humidity since 1973

Species	Humidity conditions of pollen exposure to SO_2	Reference
eggplant	moist	Taniyama and Umon 1973
Tradiscantia virginiana	saturated	Ma. et al. 1973
Populus deltoides	dry and moist	Karnosky and Stairs 1974
Pinus resinosa	dry and moist	Karnosky and Stairs 1974
Pinus nigra	dry and moist	Karnosky and Stairs 1974
Picea pungens	dry and moist	Karnosky and Stairs 1974
Tradiscantia paludosa	saturated	Ma and Khan 1976
Lilium longiflorum	moist	Masaru et al. 1976
Cicer arietenum	dry and moist	Varshney and Varshney 1981
Nasturtium indicum	dry and moist	Varshney and Varshney 1981
Petunia alba	dry and moist	Varshney and Varshney 1981
Tradiscantia axillaris	dry and moist	Varshney and Varshney 1981
Lepidium virginicum	wet	DuBay and Murdy 1983a

Another in vivo study (Murdy and Ragsdale 1980) of SO_2 effects on reproduction in *Geranium carolinianum* L. suggested that in vitro SO_2 effects on pollen may correspond to in vivo effects on stigmas under high RH conditions. The resultant reduced pollen germination and initial tube growth may reduce seed set. Such an in vivo reduction of pollen germination after fumigations of SO_2 at the time of pollination was shown to reduce seed set at 90% RH in *Geranium carolinianum* (DuBay and Murdy 1983b).

Although acid inhibition of pollen activity has been known since the work of Dopp (1931), other investigations have also noted the importance of acidity in pollen germination and tube growth since that time (Cooper 1939; Brewbaker and Majumder 1961; Kratky et al. 1974). In addition, Iwanami et al. (1978) attributed pollen inviability in beehives to acidity.

Masaru et al. (1980), however, finally verified the importance of H^+ ion inhibition of pollen tube growth by assaying *Camellia* pollen in three inorganic acids and their corresponding ammonium salts. The *Camellia* pollen was markedly inhibited at pH 3.2, which demonstrated possible implications of regional acid precipitation on plant reproduction.

The above observations, together with the information on trace metal ion effects on pollen activity (Masaru et al. 1980; Arvind and Malik 1976; Strickland and Chaney 1979), prompted investigations into the in vitro responses of pollen from a wide range of forest species to acidities and trace metal ions present in ambient rainfall in eastern Canada. An account of the effects of soil differences at site of pollen collection on pollen response to pH, together with in vivo effects of simulated acid rain on stigma receptivity, will be presented.

IN VITRO ASSAYS

Sensitivity to pH

To determine the response of pollen to pH, a wide range of forest species' pollen was sampled from various individuals of potentially sensitive species. These species were selected using the criteria described in Table 2. Fresh pollen was used in the assays, except from the pines, which were stored from two weeks to two years over silica gel at -15°C. The pollen was assayed in 50-µL standing drop cultures in a random block design of five blocks in a moist chamber at 24 ± 2°C. The culture medium was essentially that of Brewbaker and Dwack (1963), adjusted to pH 5.6, 4.6, 4.0, 3.6, 3.0 and 2.6 with dilute sulfuric acid and ranging in sucrose concentration from 0.6 to 20.0% w/v, depending on the osmotic requirements of the pollen. For further methods see Cox (1983). After appropriate transformations the pollen germination and tube length data were subjected to analysis of variance (ANOVA) and multiple-range tests (Tables 3 and 4). LD_{50} dosages of pH were also computed for the germination data (Fig. 1). Pollen of the 12 species tested wassignificantly influenced by pH treatments ($P<0.01$). Two-thirds of the species had pollen that was inhibited in germination ($\alpha=0.05$) at pH 3.0 (1000 µeq H^+C^{-1}) but few effects were observed at pH 4.6 (25 µeq H^+C^{-1}. The species ranking of pollen sensitivity to acidity (Tables 2 and 3), where rank was determined according to the point on the pH gradient at which significant ($\alpha= 0.05$) inhibition of the responses occurred, resembled that produced using LD_{50} information on pollen germination (Fig. 1). The LD_{50} dosage is the computed dosage of pH that would produce a 50% probability of response (failure to germinate) of the pollen grains. For the sake of brevity, the latter toxicological approach will be used to describe the rank of broad sensitivity groups of species common to both types of analysis. Broad-leaved canopy tree species were the most sensitive, with LD_{50} dosages of pH 3.95 to 3.63, together with the open habitat herb *Oenothera parviflora* L. and the sensitive *Pinus strobus* L., which a LD_{50} dosage pH 3.6. Next in sensitivity were the species of the understorey and ground flora, whose values for LD_{50} ranged from pH 3.58 in *Maianthemum canadense* Desf., to pH 3.14 in *Diervilla lonicera* Mill. These species were followed in sensitivity by the three remaining conifers with LD_{50} dosages that ranged from pH 3.19 for *Pinus banksiana* Lamb. to pH 2.94 for *Tsuga canadensis* (L.) Carr.

Species	No. of Populations	No. of Individuals
Acer saccharum	1	1
Populus tremuloides	3	3
Oenothera parviflora	2	3
Betula papyrifera	1	1
Pinus strobus	2	2
Maianthemum canadense	1	1
Trillium grandiflorum	2	2
Prunus pennsylvanica	1	2
Diervilla lonicera	1	2
Pinus banksiana	1	1
Pinus resinosa	1	1
Tsuga canadensis	1	2

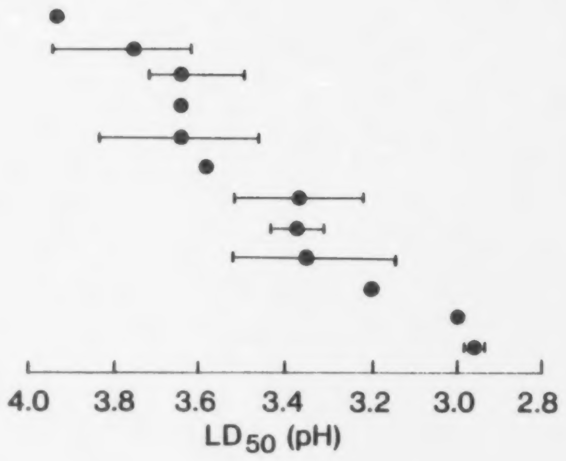

Figure 1. The means and ranges of LD_{50}s for germination responses of pollen sampled from individual forest species cultured at various initial pHs.

Table 2. Some criteria for the identification of plant species potentially sensitive to acid rain effects on reproductive processes

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Pollen

a. Low viability.
b. Small pollen ovule ratio.

Flower

a. Orientation and architecture do not protect stigma or anthers from rainfall at anthesis.

b. Short synchronous flowering season where a large percentage of flowers will experience the effects of an acid rain event at the time of pollination.

Breeding system

a. Not cleistogamous or apogamous.

Sensitivity to Combinations of pH and Cadmium

These experiments were carried out using the same experimental procedures as described for the pH experiments except that for every pH there was a series of four or five metal concentrations in a factorial design of five blocks.

Cadmium is a long range transported air pollutant found in rainfall and ranges in concentration from 0.48 to 2.3 µg L^{-1} in urban areas, 0.08 to 46.0 µg L^{-1} in rural areas and 0.004 to 0.639 µg L^{-1} in remote areas (Galloway et al. 1982). The combined effects of cadmium and pH on *Trillium grandiflorum* (michaux) Salisb. pollen were examined using cultures of pH 5.6, 4.6, 3.6 and 2.6. At each pH, four concentrations of cadmium (0 µM, 1.0 µM, 20 µM and 50 µM) were used, and each treatment was replicated five times.

Although these cadmium concentrations are in excess of those expected in rain, the 1.0 µM (112 µg L^{-1}) concentration does approach the maximum expected to accumulate on vegetative surfaces as a result of both dry and wet deposition (Lindburg et al. 1981). The response surfaces for pollen germination and tube growth are shown in Figure 2. Analysis of variance revealed significant pH and cadmium effects ($P<0.01$ and $P<0.001$ respectively) with significant interaction terms ($P<0.05$). The interaction was in part due to a synergism at pH 3.6 and 50 µM cadmium. However, at lower, more realistic levels of the metal at pH 3.6, a stimulation of germination and tube growth occurred. The inhibitory effect at the pH levels used was more marked than the effect of the cadmium and was stimulatory to pollen germination at pH 4.6. At pH 3.6, effects were similar to those at pH 5.6 except for the high cadmium concentrations. The pH 2.6 treatments, however, were all highly inhibitory ($\alpha = 0.05$) to both germination and tube growth.

Table 3. The effect of initial culture pH on the percent germination (arcsin) of pollen collected from various individuals of 13 forest flora species (values are means of five replicate cultures)

Species	Location	Individual	Mean length (μm Log$_e$) for each pH					
			pH 5.6	pH 4.6	pH 4.0	pH 3.6	pH 3.0	pH 2.6
Oenothera parviflora	Erindale, Ont.	i	57.0	45.2*	45.5*	29.4*	0.0*	0.0*
Oenothera parviflora	Muskoka, Ont.	i	39.4	36.3	37.5	22.2*	16.3*	6.3*
Oenothera parviflora	Muskoka, Ont.	ii	40.8	39.7	29.8	20.1*	6.5*	1.0*
Acer saccharum	Erindale, Ont.	i	14.9	15.6	5.3	3.7*	0.0*	0.0*
Populus tremuloides	Toronto, Ont.	i	47.5	42.0	58.8	21.3*	0.0*	1.6*
Populus tremuloides	Toronto, Ont.	ii	44.0	52.9	45.5	29.0*	2.3*	0.0*
Populus tremuloides	Toronto, Ont.	iii	30.3	32.7	23.0	9.0*	0.0*	0.0*
Betula papyrifera	Burt Lake, Ont.	i	30.6	38.7	38.7	14.9*	4.7*	5.8*
Pinus strobus	Wisconsin, USA	i	51.0	55.9	36.3	25.2*	2.3*	0.0*
Pinus strobus	Pointe Platon, Que.	i	53.3	56.6	48.5	41.4	10.0*	0.0*
Trillium grandiflorum	Muskoka, Ont.	i	56.7	70.1+	-	42.8	-	1.7*
Trillium grandiflorum	Halton County, Ont.	i	67.3	66.8	77.5	58.7	29.9*	4.2*
Maianthemum canadense	Burt Lake, Ont.	i	56.2	58.5	42.2	27.7	0.0*	0.0*
Prunus pennsylvanica	Burt Lake, Ont.	i	48.7	47.9	49.4	41.7	5.4*	3.5*
Prunus pennsylvanica	Burt Lake, Ont.	ii	25.2	34.1	23.3	20.0	11.0	0.0*
Diervilla lonicera	Burt Lake, Ont.	i	31.4	44.0	30.3	27.1	0.0*	0.0*
Diervilla lonicera	Burt Lake, Ont.	ii	21.2	30.0	30.6	23.3	1.8	0.0*
Picea mariana	Burt Lake, Ont.	i	11.8	13.8	7.0	10.3	7.9	0.0*
Pinus banksiana	Burt Lake, Ont.	i	25.4	28.6	26.5	19.0	16.3	12.7*
Tsuga canadensis	Erindale, Ont.	i	63.7	73.5	68.9	54.5	47.4	0.0
Tsuga canadensis	Erindale, Ont.	ii	61.8	75.6	75.4	69.6	51.6	1.6*
Pinus resinosa	Nova Scotia	i	68.1	55.8	57.3	65.5	62.9	0.0*
Pinus resinosa	Muskoka, Ont.	i	13.5	18.8	26.8+	16.0	12.8	1.8

* Means significantly lower than those of the pH 5.6 treatment ($\alpha = 0.05$ for a Duncan's Multiple Range Test).

+ Means that show a significant increase with a decrease in pH ($\alpha = 0.05$ for a Duncan's Multiple Range Test).

Table 4. The effect of initial culture pH on mean length (µm Log_e) of the longest (90th percentile) pollen tubes of pollen collected from various individuals of 13 forest flora species (values represent means of five replicate cultures)

Species	Location	Individual	Mean length (µm Log_e) for each pH pH 5.6	pH 4.6	pH 4.0	pH 3.6	pH 3.0	pH 2.6
Acer saccharum	Erindale, Ont.	i	3.6	3.5	0.7*	0.5*	0.0*	0.0*
Populus tremuloides	Toronto, Ont.	iii	6.2	5.5	4.5*	1.7*	0.0*	0.0*
Populus tremuloides	Toronto, Ont.	i	6.6	6.6	6.5	2.9*	0.0*	0.0*
Populus tremuloides	Toronto, Ont.	ii	6.5	6.7	6.5	4.1*	0.5*	0.0*
Betula papyrifera	Burt Lake, Ont.	i	2.7	2.8	2.5	0.6*	1.0*	1.3*
Oenothera paviflora	Erindale, Ont.	i	5.7	5.3	5.2	4.8*	0.0*	0.0*
Oenothera paviflora	Muskoka, Ont.	ii	5.2	4.8	4.5	3.0*	1.0*	0.0*
Oenothera paviflora	Muskoka, Ont.	i	4.7	4.5	3.8	3.1	2.2*	1.0*
Diervilla lonicera	Burt Lake, Ont.	ii	4.4	4.2	4.0	2.2*	0.1*	0.0*
Diervilla lonicera	Burt Lake, Ont.	i	4.5	4.7	4.9	3.1	0.0*	0.0*
Trillium grandiflorum	Muskoka, Ont.	i	4.8	5.1+	-	4.0*	-	0.6*
Trillium grandiflorum	Halton County, Ont.	i	4.7	4.3	4.6	3.8	1.8*	0.8*
Pinus strobus	Wisconsin, USA	i	4.5	4.6	3.8	3.2	0.3*	0.0*
Pinus strobus	Pointe Platon, Que.	i	4.9	4.8	4.8	4.3	1.6*	0.0*
Maianthemum canadense	Burt Lake, Ont.	i	5.9	5.2	5.3	4.6	0.0*	0.0*
Tsuga canadensis	Erindale, Ont.	i	6.8	6.5	6.7	6.4	4.6*	0.0*
Tsuga canadensis	Erindale, Ont.	ii	6.8	6.9	6.8	6.7	4.2*	0.3*
Prunus pennsylvanica	Burt Lake, Ont.	ii	3.9	2.1	3.0	2.2	3.5	0.0*
Picea mariana	Burt Lake, Ont.	i	2.7	2.7	2.2	2.3	2.7	0.0*
Pinus banksiana	Burt Lake, Ont.	i	2.3	2.4	2.1	1.9	2.0	1.4*
Pinus resinosa	Nova Scotia	i	4.1	3.8	3.3	3.9	3.9	0.0*
Pinus resinosa	Muskoka, Ont.	i	1.6	2.2	3.2+	2.5	1.4	0.7
Prunus pennsylvanica	Burt Lake, Ont.	i	3.3	3.7	2.6	2.8	0.5	0.0

*Means significantly lower than those for the pH 5.6 treatment ($\alpha = 0.05$ for a Duncan's Multiple Range Test).

+Means that show a significant increase with a decrease in pH ($\alpha = 0.05$ for a Duncan's Multiple Range Test).

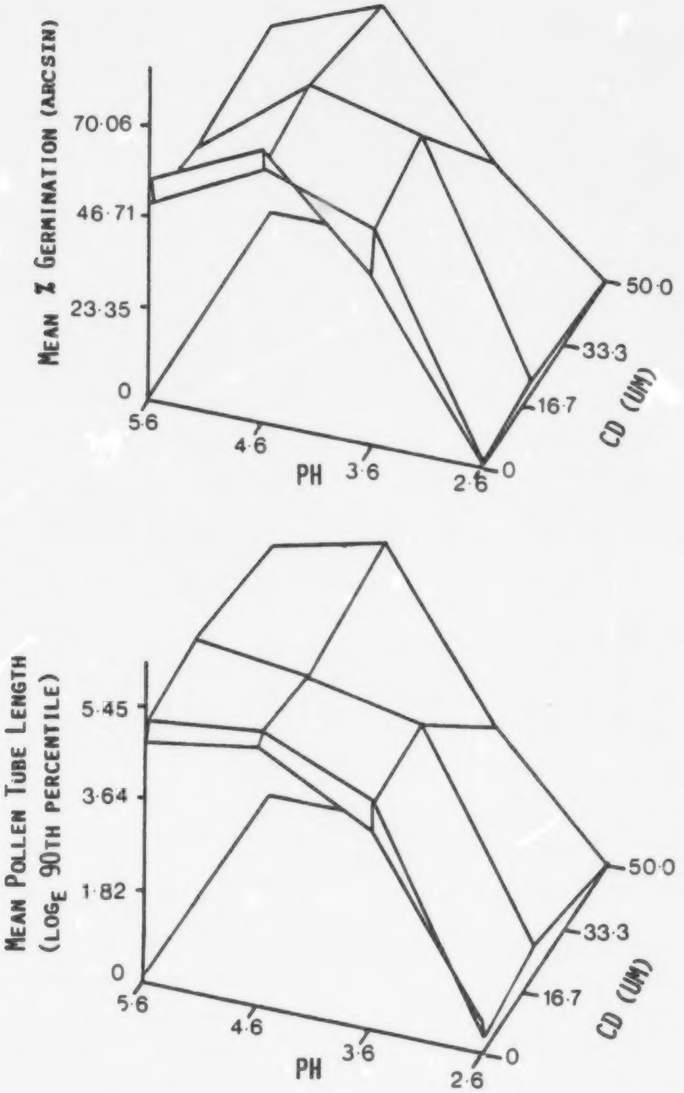

Figure 2. The effects of acidity of liquid culture media on *Trillium grandiflorum* pollen in the presence of different cadmium concentrations (means derived from five replicates).

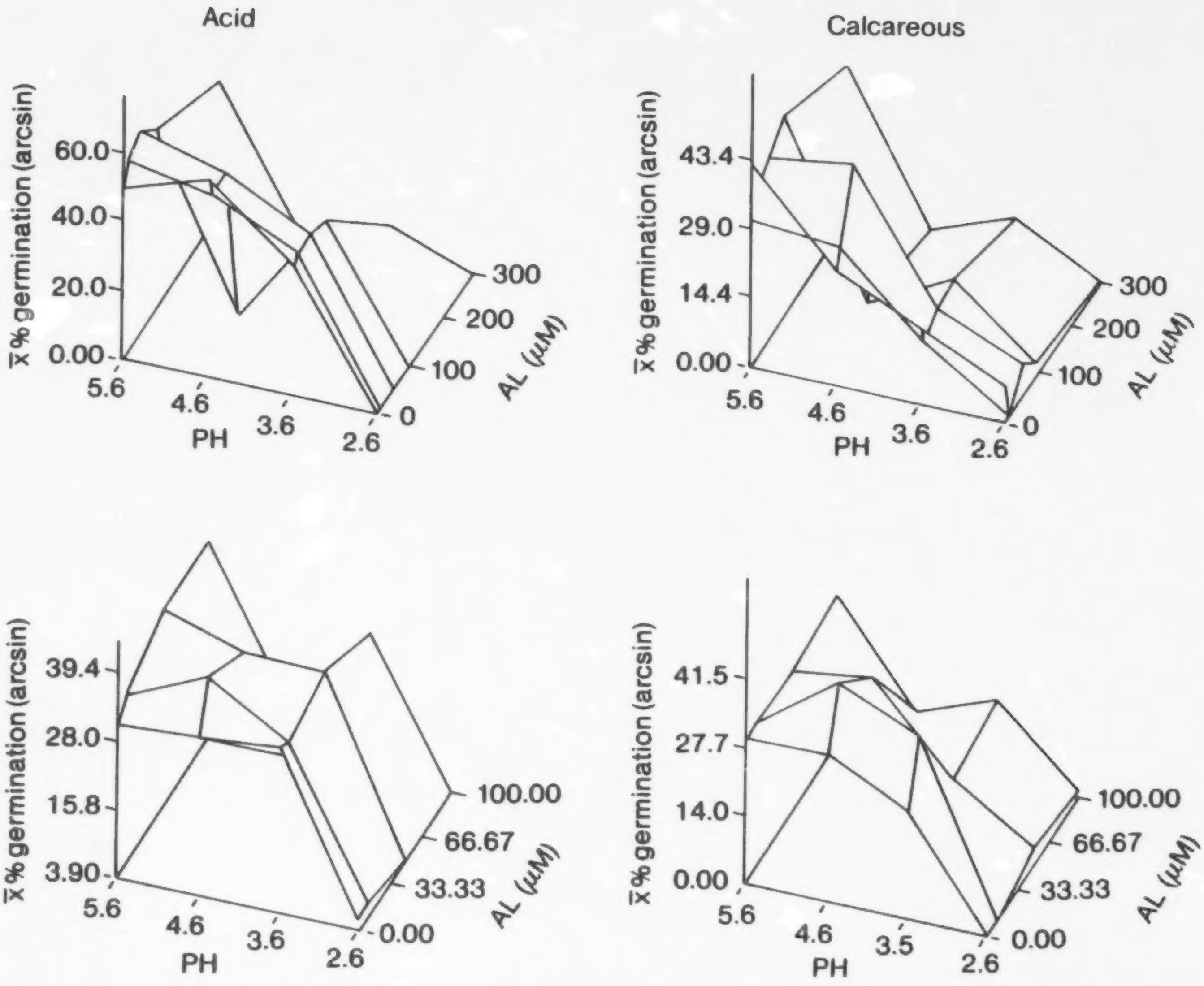

Figure 3. Responses of pollen germination from two individuals of *Pinus strobus* from an acid and a calcareous soil population to combinations of pH and aluminum concentrations.

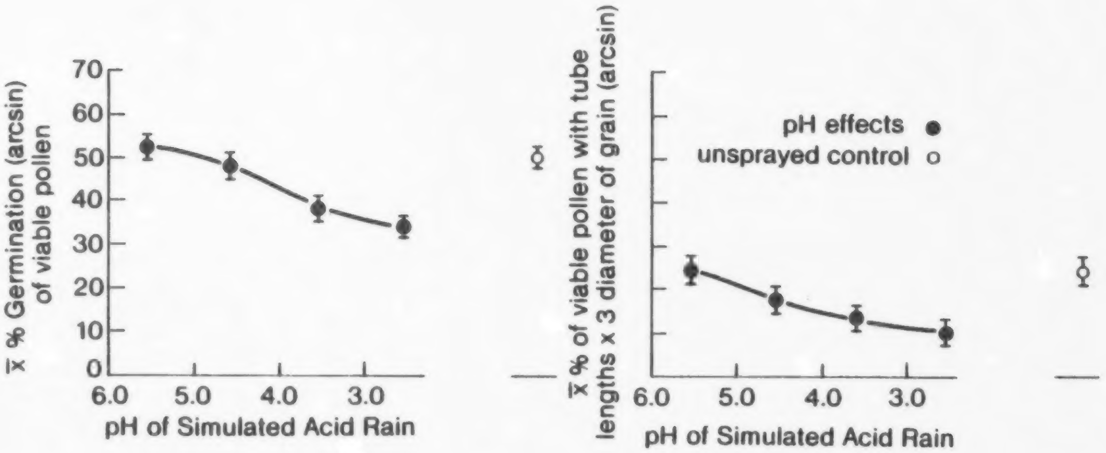

Figure 4. The effects of simulated acid rain on stigma receptivity of a Muskoka population of *Oenothera parviflora* in the field (means ± SE derived from eight replicate stigmas).

Sensitivity to Combinations of pH and Aluminum

Plants are known to vary in their response to soil pH (Russell 1973) and may show differential adaptation to various soil types within their range (Snaydon 1962). These facts, together with the suggestion that pollen tolerances may reflect the tolerances of their sporophytes (Feder 1981; Murdy 1979) and the current interest in pH/Al interactions and toxicity, prompted an investigation into their combined effects on *Pinus strobus* pollen collected from sites with calcareous and acid soils. Pollen was sampled from sites no further apart than 2.5 km in the Little Current area, Manitoulin, Ontario, and was air-dried and stored over silica gel at -15°C for no more than two weeks.

The factorial experiments were both carried out using the same techniques described for the former in vitro experiments. However, due to the length of incubation (140 h), 30 ppm of mycostatin and chloramphenicol were added to the 20% sucrose medium to prevent proliferation of bacteria and fungi. Two pairwise comparisons were made. The first was a 4 x 5 factorial with five replicates for each of the four pH treatments (pH 5.6, 4.6, 3.6 and 2.6), five aluminum concentrations were used (0, 10, 50, 100 and 500 µM Al). The second comparison used pollen from two different individuals in the populations. These were assayed under the same conditions except that the 500 µM Al treatment was omitted.

The pollen response surfaces for mean percent germination (arcsin) are shown in Figure 3. Again, ANOVA indicated significant pH ($P<0.0001$) and aluminum ($P = 0.56$ to 0.0001) effects and significant interaction terms ($P = 0.05$ to 0.0001). A large synergism is seen at pH 4.6 with concentrations of aluminum greater than 50 µM.

Apart from the synergistic interaction, the general slope of the response surfaces indicates the more susceptible nature of the pollen sampled from calcareous genotypes. These preliminary observations support the hypothesis that pollen tolerance could reflect edaphic tolerances of the pollen donors selected under the calcareous and acid soil conditions.

IN VIVO STIGMA RECEPTIVITY AND SIMULATED ACID RAIN

Stigma receptivity tests were carried out using field simulations of precipitation events of depth ≈0.26 cm using calibrated hand sprays. Simulant solutions at pH 5.6, 4.6, 3.6 and 2.6 were applied to virgin receptive stigmas (eight replicates for each treatment) of emasculated flowers of a Muskoka population of *Oenthera parviflora* whose petals had also been removed to stop natural pollination. Twenty minutes later, known pollen loads (range 40-80) were placed on each stigma with a needle and the aid of a watchmaker's eyepiece. Control stigmas were left unpollinated and showed no natural pollination. Stigmas were left for five hours before excision and fixation. Forty-five stigmas were stored individually in 1:1 acetic acid and ethanol. The individual stigmas were later stained in cotton blue (Datta and Wong 1967), squashed and mounted in 80% lactic acid. The percentage of potentially viable pollen (darkly stained contents) that 1) germinated and 2) produced tubes long enough to penetrate the stigma (i.e., 3 x diameter of grain) was recorded (Fig. 4). Analysis of variance indicated that acid rain simulants caused a significant ($P <0.01$) reduction in stigma receptivity using both criteria, and that pH 3.6 and 2.6 treatments significantly ($\alpha= 0.05$) reduced receptivity compared with pH 5.6 and unsprayed treatments. The LD_{50} dosages of pH computed for viable pollen that 1) failed to germinate and 2) failed to produce tubes long enough to penetrate the style were pH 3.45 and pH 4.55 respectively.

DISCUSSION

The in vitro assays suggest variation among species in the susceptibility of their pollen to pH. In broad-leaved species, pollens of canopy trees were more susceptible to pH than those of the understorey and ground flora perennials. As a group, conifers seem to have pollen more tolerant of acidity, with the exception of *P. strobus*. The more generalized pollen sensitivities described in this study resemble the sensitivity of similar groups of species described by Jacobson and Van Leuken (1977) and by Evans (1980) for foliar sensitivity to simulated acid rain. It was suggested, however (Cox 1983), that for a fuller understanding of the relative sensitivities of reproductive processes of forest plants to acid precipitation, they must be related to the species position in the canopy strata, as well as to the composition of the canopy due to demonstrated differences in pH of ambient rainfall and throughfall (Richter and Granat 1978).

The combined in vitro effects of pH and cadmium on *T. grandiflorum* pollen confirmed its sensitivity to pH. However, the only significant cadmium effects were demonstrated at 50 µM (5.62 mg L^{-1}) Cd at, or below, pH 3.6. Lower, more realistic cadmium concentrations of 1 µM (0.1 mg L^{-1}) or 20 µM (2.25 mg L^{-1}) were stimulatory, if anything, to pollen function. These results indicate that Cd may be added to Pb and Mg cations found to be stimulatory to pollen at concentrations found in acid precipitation (Masaru et al. 1980); or, as in this case with Cd, at concentrations in excess of that expected to accumulate due to wet and dry deposition (Lindburg et al. 1981).

The combined action of aluminum and pH on germination of *P. strobus* pollen indicates both Al and pH effects, as well as a significant interaction. The synergistic interaction on pollen germination (Fig. 3) may be due to a change in free aluminum species in the culture to a more toxic form from pH 5.6 to 4.6, i.e., $Al(OH)_2^+$. At pH 3.6, however, reduced toxicity may be due to increased complexation of trivalent aluminum (Al^{3+}) in the 20% sucrose medium (Burrows 1977). This indicates that in vitro assays of pollen may provide a useful way to examine aluminum toxicology of higher plants related to soil acidification.

Of more relevance to the direct effect of acid precipitation is the apparently greater pH sensitivity of the *P. strobus* pollens sampled from calcareous sites, compared with those from acid sites. This supports the view that sporophyte tolerances are reflected in their pollen and may indicate that reproduction in *P. strobus* adapted to calcareous soils may suffer more in terms of acid rain effects on their pollen than for populations associated with acid soils.

The direct exposure of pine pollen to acidic rain, fog, or mist may occur when pollen adhere to the stigmatic tissue of the receptive cone scales. In addition, pine pollen is exposed to the accumulated acidity deposited on the cone scale from both wet and dry deposition during the exudation of the pollination droplet from the micropyle.

The reduced stigma receptivity of *O. parviflora* is the first such observed in vivo effect due to simulated acid rain, although similar effects caused by SO_2 fumigations have been observed by DuBay and Murdy (1983a,b). This supports the suggestion of Evans (1979) and Jacobson (1980) that reproductive structures exposed to acid precipitation may suffer direct damage.

Comparison of in vitro and in vivo pollen sensitivities in *O. parviflora* indicates that, in both cases, pollen germination was inhibited by pHs equal to, or lower than, 3.6. LD_{50} dosages, however, indicate that in vivo germination may be somewhat less affected by initial pH than in vivo experimentation, which may reflect the extra buffering capacity of the stigmatic surface. This buffering explanation is also discussed by Karnosky and Stairs (1974) and DuBay and Murdy (1983a) in relation to SO_2 effects on pollen. The increased degree of in vitro inhibition of germination over the in vivo response, however, may be due to the heterogeneous or spotty distribution of acidity on the stigmatic surface. The LD_{50} dosages of the two in vivo pollen responses measured for *O. parviflora* were pH 4.66 and 3.45 for the mean percentage (arcsin) of grains that produced tubes >3 times their diameter and the mean percentage (arcsin) that produced tubes >1 diameter respectively. This evidence indicated that the critical stage of stigmatic penetration was more sensitive to simulated acid rain than germination of the pollen on the stigma.

Overall the results suggest that the threshold of response to pH of the various pollens tested, both in vitro and in vivo, has been exceeded by the pH of ambient rainfall in northeastern North America. Rain events approaching pH 3.0 already occur in southern Ontario (Chan 1982). Daily precipitation pH at Longwoods, near London, Ontario, had percent frequencies of 0.98, 1.96 and 5.88 for pH 3.0 to 3.25, pH 3.25 to 3.50 and pH 3.5 to 3.75 respectively for 1981 (Chan 1982, pers. commum.). The effect of these low pH events at the time of pollination is likely to reduce seed set in at least the more sensitive species, as similar pollen inhibitions caused by SO_2 fumigation have been demonstrated (Murdy 1979; Murdy and DuBay 1981b). Acid rain effects on seed set, however, are currently under examination in a variety of species.

Reductions in pollen viability caused by air pollution, be it SO_2, O_3, acid rain or various combinations, may be of special significance to reproduction in boreal forest herbs where fecundity may already be low because of pollination limitation. Barrett and Helenurm (1980) were able to increase fecundity of 11 out of 12 understorey boreal forest herbs by controlled hand pollination, as compared with open pollinations. Fecundity of only three of the herbs in this study was resource limited (Table 5).

Finally, this work indicates that a full understanding of the responses to acid precipitaiton of native flora reproduction and possibly seed quality and yield in forestry and agriculture can only be brought about by the detailed examination of the reproductive processes under field simulations, where direct and indirect effects can be assessed.

Table 5. Factors regulating fecundity in boreal forest herbs

	Fecundity[1]			Pollinator	Pollinator	Resource
Species	low	med.	high	dependent	limited	limited
Aralia nudicaulis			+	+ +		
Chimaphila umbellata		+		+ +	+	
Clintonia borealis		+		+ +	+	
Cornus canadensis	+			+ +		+ +
Cypripedium acaule	+			+ +	+ +	
Linnaea borealis		+		+	+	
Maianthemum canadense	+			+ +	+	+ +
Medeola virginiana	+			+ +	+ +	
Oxalis montana		+		+	+ +	
Pyrola secunda		+		-	+	
Trientalis borealis	+			+ +		+ +
Trillium undulatum			+	-	-	

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[1] low 0-33%, med. 33-66%, high 66-100% (source: Barrett and Helenurm, unpublished)

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DISCUSSION

Question: Could you comment on the relationship between aluminum concentration and pH as to their effects on reproductive processes?

Answer: I am not concerned with reproduction processes *per se*; it is the question of fitness of the seeds that have been used and acid rain conditions. You might get selection for tolerant pond grains to acidity and this might affect fitness in the next generation. The prime aim of the assay is to look at the effects of acidity and whether there is a differential response of the two pollen types that were gathered from the two different environments. The concentration used in the assay was selected based on its closeness to the LD_{50}. You have a choice in these assays whether to select environmental concentrations or to select concentrations from which you can determine the response most accurately and then relate back to the environmental situation. However, aluminum is so complicated and does not really relate to the cultural conditions, which were in a sucrose solution, so I thought it quite a reasonable thing to do at that sort of concentration.

Question: What was the assay medium used?

Answer: It was a Brewbaker's solution containing various concentrations of sucrose depending on what was optimal for the germination of the pollen. I thought that was a reasonable criterion to use rather than to standardize it with one sucrose concentration, because stigmatic surfaces vary according to the germination conditions of the pollen. The pollen was mostly fresh, except for the conifers which were stored at -5°C by the silica gel.

Question: Could you comment on the effect of the acid treatments on the reproductive systems of *Oenothera* and the conifers?

Answer: They are very different. For *Oenothera*, the effect is directly on the stigmatic surface where germination occurs very quickly. In pines, the exposure to acid rain on the stigmatic surface would be the most important. The initial uptake of the water containing the aluminum or hydrogen ions and their direct effect on the membranes would presumably be the most important. This can occur before pollen drop formation which brings the pollen back into the micropylar reception area of the pollen and where germination may or may not occur. Presumably here the concentrations of this acidity would not remain effective for the year that it takes before resumption of pollen tube growth and fertilization in the next year. It is the initial effect of the uptake of the water on the stigmatic surface that affects pollen viability in this case.

Interaction of Forest Canopies with Air Pollutants — Processes and Rates

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ABSTRACT

A forest canopy acts as a simple receiving surface only for wet and dry deposition of particles subjected to gravity, like rain droplets, snow flakes and dust particles. The deposition rate of water-soluble gases like SO_2, NO_x and NH_3, as well as of aerosols and cloud droplets, depends on their size and their properties, including the metabolic activity of the receiving surface. Such processes may be summarized as interception deposition (ID). No approach or measurement exists on the rate of ID of NO_x and NH_3. The dry deposition of SO_2 depends greatly on the stomata opening, the wetness of the canopy and its acid buffer rate. Fog and wet snow can increase dry deposition of SO_2, due to the provision of a wet surface. In areas where deep-reaching clouds come in contact with the canopy, a considerable increase in deposition of acidity, sulfate and heavy metals can occur, due to the filtering effect of the canopy. The measurement of deposition rates with the aid of artificial surfaces (e.g., wet/dry samplers) can result, therefore, in considerable underestimation. Under the conditions of exposed forests, the flux balance of the canopy seems to be the only way to arrive at realistic total deposition rates for a great variety of air pollutants.

Luncheon Address
The Power of Words — Some Examples

Dr. Marcel Lortie
Université Laval, Québec

June 15, 1983

Ladies and gentlemen,

I would like to begin by expressing my respect for you research workers who are attempting to shed light on the complex relationships that exist, or may exist, between acid precipitation and the reaction of plants, particularly forest trees. Regardless of the context imposed by society, the problem in itself is difficult to address; it requires the development of hypotheses that are difficult to confirm or refute. I know what I am talking about because I worked for 10 years or so trying to solve – with little success – a problem referred to as birch decline. I was frustrated by situations with which you must be familiar. Today, I sum up my experience on birch decline by saying that I know what it is not, but I do not know what it is.

After agreeing to speak to you today, I quickly realized that I was ill-equipped to address the problems facing you. However, in listening to some of you speak, I did not always feel ignorant of your concerns. At times, I even had the impression that I had already heard what you are saying.

In 1953, as a forestry student, I had a summer job in forest pathology with the Quebec City office of the federal Department of Agriculture's Forestry Biology Division, an organization which later joined with the Forestry Branch of the Department of Northern Affairs and Resources to form the core of the Canadian Forestry Service. A young researcher named Lee A. Paine had just joined the laboratory, which was to become the Laurentian Forest Research Centre.

He had arrived from Europe and his first project – in fact, his only project in Quebec City before he moved to Berkeley in 1959 – was to find the cause or causes of the failure of the white spruce plantations in Grand'Mère. From time to time, he and I talked about the problem he was studying. I even had the privilege of conducting soil analyses for him through a contract at Laval University.

His hypothesis was that ecological factors contributed to soil acidification to a point where certain minerals, such as aluminum, became assimilable and thereby toxic. Trees could not survive some of the forms these minerals took. Projects to confirm this hypothesis, he told me, were being developed in Germany. I have a feeling that in 1953 or 1954, that is how some of you would have talked about aspects of the problem you are studying today.

Obviously Lee Paine did not talk about acid rain. Today's problem, some will say, is much more important than the small plantations at Grand'Mère.

Yet, is the scientific process more important because we have a problem that affects the entire continent? Is research on the properties of germanium crystals less worthwhile than research on transistors because the latter have had and still have potential economic applications? And yet, without the first, the second would hardly have been possible.

Is your research on acid rain more important than when those of you with Environment Canada were working on the LRTAP program (Long Range Transport of Air Pollutants)?

What I would like to talk to you about today is the importance of words, the role of words, the influence of words. Those of you who have been in the field long enough will remember how difficult it was to secure funding for a fraction of the LRTAP project. As soon as words that conjure up an image, catchy words like "acid rain," appeared in the news media, an agency that analyses the content of media, particularly the written press, was to inform the federal authorities of the future impact of these words. Politicians and those close to political power, senior officials, fast fell victim (willing victims in some cases) to the new expression. But try to explain to Treasury Board (this was before the days of ministries of state for development) the value of the research conducted under the LRTAP program compared with research that could in future help destroy this alien monster, which could corrode, or I should say, was corroding our buildings and our cars and turning our lakes into vinegar.

Some felt that the hype being created about the words "acid rain" could be harmful to scientific rigor and have since used the expression "acid precipitation," which at least clearly indicates that the phenomenon is, in our climate, just as important in winter.

Rallying the support of politicians and senior officials in the fight against acid rain depended, and still depends, on basic knowledge of the phenomenon, on in-depth research.

However, the urgent need for immediate action generated by the feelings aroused by the words "acid rain" must have prompted some of them to suggest the results that the researchers should obtain and to establish a time limit for the research. Unfortunately, some professionals wanted to please their bosses. I have read, as you have, statements where major conclusions were drawn from unverified hypotheses. Like you, I have also read such phrases as: "Although adverse effects have not been measured, we cannot disbelieve that . . . ."

This type of statement is indiscriminately quoted with increasing frequency. And that is the source of the problem. The current climate favors either alarmism or smug indifference. There is a market for both alarmist words and reassuring words. At times, unqualified statements, sometimes false, are made. Of course, this is not true of acid rain alone. Last week, for instance, a forester who was asked why he supported the aerial spraying of herbicides replied more or less as follows: "The red-osier dogwood poses a problem for regeneration. Mechanical slashing causes regrowth of the slash. Only herbicides work." The journalist apparently added that he himself had consulted *La Flore Laurentienne* by Marie-Victorin, who had written that the dogwood formed associations of great ecological importance. So much for the forester who is ignorant of ecology. However, the forester was talking about the red-osier dogwood, whereas the journalist had read about another dogwood species, the bunchberry. But no matter, six or seven million people got the message that foresters know nothing about ecology. But the journalist does.

Another example? We talk about forest management, which in French is "aménagement forestier." Some people, like me, try to remember the meaning of the word management, namely the orderly scheduling of harvesting in time and space. But it is in vain. As someone recently told me, the word "aménagement" contains the word "ménage," which means housework. Therefore, to manage is to clean house. We hear such claims as "there are never budworms in a properly managed forest" (I know of no valid research that could even suggest such an idea). We are shown photographs of forests where all regrowth has been removed and we are told: this is a well-managed forest!

I agreed to come and speak to you today to tell you what I expect of scientists like you and to ask you to continue to act like scientists, even if the temptation to take a social or economic stand with the knowledge you have is strong. Don't misunderstand me. Scientists, like everyone else, have a right to political choices. But science is not political.

I recently read that one of the problems associated with environmental impact assessments is that assessment and science are often confused. The author reminds us that an impact assessment is a planning process, and therefore political, and that there is nothing scientific about it, except for the accuracy of the basic data. Similarly, in fields of research like acid precipitation, the basic data must be accurate. And if politicians wish to use these data, they should do so; but they should at least use accurate, rigorous data.

I must sound like a preacher. That is not my intention. Rather, I am concerned about the reputation of researchers and the intrinsic authenticity of research.

I suspect that some of you are saying to yourselves: Good, he's almost done. But what about Lee Paine? Was he able to establish a relationship between the acidity of the soil at Grand'Mère and the deterioration of the trees? Well, with the methods then available he had to abandon his working hypothesis and concentrate on nutrient deficiencies. In a preliminary report published in 1956, he explained that many observations appeared to suggest a combined effect of nutrient deficiencies and climatic factors. But he could not resist stating the following: "Toxic iron, aluminum, and manganese concentrations probably play a minor role in the development of the disease pattern."

However, in the final report of his work, published in 1960, Lee Paine made no further reference to the question of toxicity.

In closing, I would like to wish you every success in your deliberations. Thank you.

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TECHNICAL SESSION IV
EFFECTS OF ACID RAIN ON SOIL PROCESSES

Acid Rain and the Buffer Capacity of Forest Soils

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ABSTRACT

Past reviews of the effects of acid rain on soil nutrients suggest five major concerns: increased leaching losses; reduction in cation exchange capacity; accelerated weathering of soil minerals; mobilization of toxic elements; and changes in soil biota. These effects assume that acid precipitation accelerates soil acidification. We studied the capacity of forest soils to buffer H^+ in precipitation by adding H^+ and OH^- to soil samples from forested sites in Maine, New Hampshire, and Connecticut. The change in pH for a unit addition of H^+ or OH^- is nearly independent of pH for these soils. Buffer capacity ranged from 5 to 15 mmol (H^+) kg^{-1} pH^{-1} in our mineral soils, and from 20 to 100 mmol (H^+) kg^{-1} pH^{-1} in our forest floors. The buffer capacity was closely related to organic content. In a worst case situation, in which mitigating factors are neglected, our buffer capacity values indicate that a change in pH of one unit in the forest floor would require an addition of only 2 to 10 kmol (H^+) ha^{-1}, while a change of one unit in the mineral soil would require 30 to 50 kmol (H^+) ha^{-1}. These data suggest that forest soils may not be the super buffer that is sometimes depicted.

INTRODUCTION

Several recent and thorough reviews discuss the potential impacts of acid rain on soils (Alexander 1980; Bache 1980; Frink and Voigt 1977; Johnson et al. 1982; McFee 1978; Tamm 1976). These demonstrate that several effects of acid rain can be hypothesized based on current knowledge of soil processes. However, quantitative and qualitative data to back up the hypotheses have been slow in developing. Also, the issue is clouded by the possibility that acid rain may have beneficial as well as adverse effects on soils (Andersson 1982). The same information is sometimes used to demonstrate either possibility. The obvious conclusion at this time is that actual effects of acid rain on soils remain largely unresolved.

On the basis of these ideas we believed there was little to be gained by preparing another review paper. In searching for a different approach for our paper, we noted that previous reviews suggested at least five major concerns regarding the effects of acid rain on soil nutrients: increased leaching losses; reduction in cation exchange capacity; accelerated weathering of soil minerals; mobilization of toxic elements; and changes in soil biota. These effects are based on the premise that acid precipitation accelerates soil acidification. Accordingly, we decided to concentrate on the ability of soils to buffer H^+ in precipitation, or to protect against changes in pH that would change the nutrient status of soils.

H^+ CYCLING

A short review of H^+ cycling in forest systems provides some perspective on buffering capacity. This can be illustrated with data from studies made at the Hubbard Brook Experimental Forest in New Hampshire (Eaton et al. 1973; Hornbeck et al. 1977; Likens et al. 1977).

Average annual precipitation at Hubbard Brook is 1300 mm at pH 4.13, resulting in an average addition of 1.0 kmol (H^+) ha^{-1} yr^{-1}. Adding this to the soil represents a worst case situation. The pH of precipitation increases during passage through the summer canopy, or when stored in the snowpack, and enters the soil at pH 4.6 to 4.8. The fate of H^+ left in the canopy has not been completely determined, so it is not possible to be specific about how much H^+ in precipitation might require buffering by soils.

Average annual streamflow at Hubbard Brook is 800 mm at pH 4.90, giving an average loss in streams of 0.1 kmol (H^+) ha^{-1} yr^{-1}. The difference of 0.9 kmol (H^+) ha^{-1} yr^{-1}, between additions at the canopy and loss in streams, suggests that the forest is a sink for a significant portion of H^+ in precipitation. However, a recent H^+ budget for the 60-year-old forest at Hubbard Brook (Driscoll and Likens 1982) shows that sources and sinks of H^+ are nearly balanced as follows:

	kmol (H^+) ha^{-1} yr^{-1}
H^+ Sources:	
Precipitation	1.0
Dry deposition	0.4
Net forest accumulation (cation uptake)	1.0
Weathering reactions	0.1
Stream alkalinity	0.1
	2.6
H^+ Sinks:	
Weathering reactions	2.1
Net forest accumulation (anion uptake)	0.3
Stream pH	0.1
	2.5

Although some of these values are based on assumptions and gross estimates, the budget suggests that the forest system, including soils, seems to buffer H^+ sources reasonably well. The difference between sources and sinks implies a net accumulation on the order of 0.1 kmol (H^+) ha^{-1} yr^{-1}. An important point is that H^+ in precipitation is a sizeable portion of the H^+ in circulation.

The acid rain problem may be intensified by some forest management practices, especially harvesting. For example, removal of the forest canopy allows precipitation to fall chemically unchanged on forest soils. As pointed out earlier, this could mean a much higher addition of H^+ at the forest floor. Also, nitrification increases dramatically in soils of harvested sites in New England. This acidifying process may combine with acid rain to accelerate acidification of soils. In the first year after clearcutting of a northern hardwood forest at Hubbard Brook, increased nitrification in soils resulted in production of H^+ that was three times the annual input in precipitation (Hornbeck et al. 1983). Disturbance to the forest floor during logging and a decline in organic material immediately after harvest (Covington 1981) may temporarily reduce the supply of bases needed to counter soil acidification. These examples point out the need to know more about the potential for soils to buffer acid additions.

DETERMINATION OF BUFFER CAPACITY

Buffer capacity cannot be satisfactorily determined *in situ*, so it is most often obtained by titrating soil samples in the laboratory. In such cases buffer capacity is defined as the H^+ or OH^- addition required per unit mass to change pH by one unit (Morris 1974). The idea of titrating soils with OH^- has long been used in agriculture to determine lime requirement. The idea of titrating soils in the opposite direction with H^+ was seldom used until the recent interest in the effects of acid rain.

It is not clear how accurately buffer capacity reflects the performance of a soil under field conditions. However, for the present, buffer capacity appears to be the best available index for evaluating the potential of soils to counter pH changes due to acid rain.

Several units are commonly used to express buffer capacity. For laboratory determinations we have chosen mmol H$^+$ (or OH$^-$) required per kilogram soil to change the pH one unit (mmol) (H$^+$) kg^{-1} pH^{-1}). When extrapolating from laboratory results to the field and using mass per unit area, we use kmol H$^+$ required per hectare to change the pH one unit (kmol (H$^+$) ha^{-1} pH^{-1}). This latter unit makes for easy comparison with acid rain. For example, 1000 mm of precipitation at pH 4.0 would add 1 kmol (H$^+$) ha^{-1}. This is close to the annual H$^+$ input in precipitation for the northeastern United States and eastern Canada, and often is referred to in acid rain studies as "the standard addition".

Study Methods

We measured buffer capacity on soil samples obtained from three sites where we are studying effects of harvest on nutrient cycles. The sites are a spruce-fir forest in central Maine, a northern hardwood forest in northern New Hampshire, and a central hardwood forest in Connecticut (Table 1). We obtained two samples for each of four or five horizons at each site. Each sample consisted of material composited from three or four soil pits. Samples had been sieved through a 6-mm screen and air dried as part of an earlier experiment.

Table 1. Soil sampling sites

Parameter	Main		New Hampshire		Connecticut	
Latitude	45° 56' N		44° 32' N		41° 24' N	
Longitude	69° 17' W		71° 03' W		72° 321 W	
Dominant tree species	*Abies balsamea* *Picea rubens* *Picea alba*		*Betula papyrifera* *Betula alleghaniensis* *Fagus grandifolia* *Acer saccharum* *Acer rubrum*		*Quercus rubra* *Quercus velutina* *Quercus prinus* *Betula lutea* *Acer rubrum*	
Soil series	Chesuncook-Telos fsl		Becket sl		Canton fsl	
Soil family	Coarse, loamy, mixed, frigid, Typic Fragiorthod		Coarse, loamy, mixed, frigid, Typic Fragiorthod		Coarse, loamy, over sandy-skeletal, mixed mesic, Typic Dystrochrept	
Horizon sampled and field pH	Oi,	3.7	Oi,	5.4	Oi, A1	4.4
	Oa,	3.4	Oa,	4.5	A2,	4.7
	E,	3.7	E,	4.7	B1,	4.8
	Bhs,	4.3	Bhs,	4.6	B2,	4.8
	Bs,	4.6	Bs,	5.1		

To begin this experiment we rewetted the soil samples to a water content approximating field capacity. The rewetted samples were stirred and incubated at 20°C for two to three weeks before acid and base additions. Actual water content of the rewetted samples was measured by oven drying two subsamples. The air drying, rewetting, and incubation are not normal procedures for determining buffer capacity; however, the air-dried samples were readily available. This summer we are continuing the work with field moist samples, but this does not yet seem to make much difference.

Three 5-g subsamples of each rewetted sample were used for acid and base additions. To one of the subsamples, 10 mL of distilled water was added to give the standard 2:1 slurry. A second subsample received 10 mL of distilled water and 0.5 mL of 0.1 N HCl. The third subsample received 10 mL of distilled water and 0.5 mL of 0.1 N NaOH. The acid and base additions were in the range of 10 to 60 mmol (H^+) kg_s^{-1}[*], depending on water content of the sample. The additions usually produced a pH change between 0.5 and 1.5 pH unit.

The pH of all slurries was determined after one day and after six days. The change in pH between day 1 and day 6 generally was less than 0.2 units and occurred for some samples in the distilled water slurry as well as in the acid or base additions. There was no obvious difference in buffer capacities determined from day 1 and from day 6 data, so we have used only day 1 values.

RESULTS

Buffer capacities calculated from the acid additions differed somewhat from those calculated from base additions for some horizons, but not for others (Table 2). Agreement implies that the buffer capacity is independent of pH within the range measured.

The buffer capacity is closely related to the organic content of these soils (Fig. 1). The mineral soils, with organic fractions less than 0.1 $g_o g_s^{-1}$, have buffer capacities of about 10 mmol (H^+) kg_s^{-1} pH^{-1}. By extrapolation, the buffer capacity of pure organic matter was estimated to be in the range of 60 to 120 mmol (H^+) kg_s^{-1} pH^{-1}. The relation of buffer capacity to organic fraction differed little among the sites.

Buffer capacities compare better among horizons when they are on a unit-area basis. The bulk densities and thicknesses of our sampled horizons differed considerably. We used data on mass per unit area from Federer (1983) to obtain buffer capacity on a unit-area basis (Table 3). Buffer capacity of the forest floor was 1.5 kmol (H^+) ha^{-1} pH^{-1} in the mor floors of New Hampshire and Maine. Despite its lower buffer capacity per unit mass, the buffer capacity of the whole mineral soil greatly exceeds that of the forest floor, and ranges from 28 to 52 kmol (H^+) ha^{-1} pH^{-1} at our sites.

DISCUSSION

Titrating forest soils with H^+ and OH^- seems to be useful for understanding the potential ability of soils to buffer acid rain. However, it is important to note that the evaluation of buffering in terms of adsorption of added H^+ can be very misleading. For example, a soil at pH 5.0 with a buffer capacity of 30 mmol (H^+) kg_s^{-1} will absorb about 99% of the H^+ from an addition of 30 mmol (H^+) kg_s^{-1}. However, the 1% of the H^+ not adsorbed is enough to change the soil pH to 4.0. It is important to look beyond H^+ absorption to the change in soil pH.

Titration curves for soil generally show a nearly linear relation between pH change and amount of acid or base added (Bolt et al. 1976). If the curve is truly linear, then the buffer capacity is independent of the pH at which it is determined. Bolt et al. (1976) show typical curves for soil materials that have buffer capacities of 20 to 40 mmol (H^+) kg_s^{-1} for mineral soils and 200 mmol (H^+) kg_s^{-1} for a peat. Our values are similar.

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[*] Subscripts on units are s — oven-dried soil, o — organic matter.

Table 2. Buffer capacities of individual samples for H^+ and OH^- additions of 10 to 40 mmol (H^+) kg_s^{-1}, which caused pH changes of about 0.5 to 1.5 pH units

Location	Horizon	Sample	Organic fraction $kg_o kg_s^{-1}$	Buffer capacity mmol (H^+) $kg_s^{-1} pH^{-1}$	Buffer capacity mmol (OH^-) $kg_s^{-1} pH^{-1}$
Maine	Oi	1	0.94	53.3	75.8
		2	0.95	53.6	80.9
	Oa	1	0.87	54.1	57.7
		2	0.92	75.1	70.1
	E	1	0.05	13.0	8.5
		2	0.05	12.0	8.4
	Bhs	1	0.13	14.9	13.2
		2	0.14	13.4	13.6
	Bs	1	0.06	11.6	7.2
		2	0.06	9.7	8.6
New Hampshire	Oi	1	0.86	92.3	170.3
		2	0.88	116.0	137.6
	Oa	1	0.49	45.5	86.4
		2	0.26	22.9	51.1
	E	1	0.02	5.2	4.9
		2	0.01	5.2	5.1
	Bhs	1	0.09	10.7	15.9
		2	0.14	11.8	23.3
	Bs	1	0.10	9.0	9.7
		2	0.09	8.0	10.3
Connecticut	Oi, A1	1	0.32	22.8	47.1
		2	0.21	18.4	29.8
	A2	1	0.08	9.0	12.0
		2	0.08	9.1	14.0
	B1	1	0.04	9.0	8.1
		2	0.04	9.2	9.2
	B2	1	0.03	10.1	7.1
		2	0.03	9.0	9.5

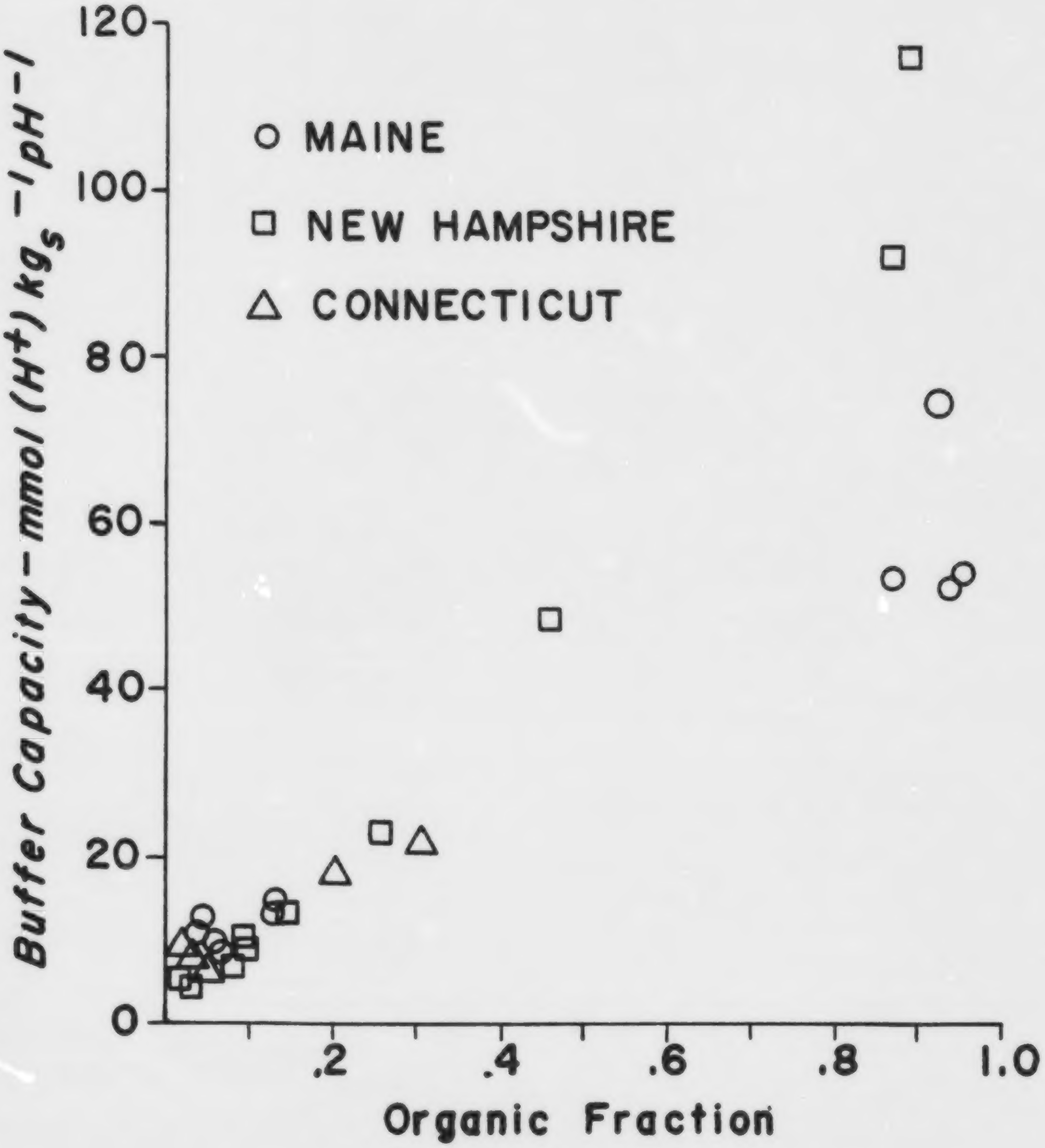

Figure 1. The relationship between buffer capacity and the organic content of soils in Maine, New Hampshire, and Connecticut.

Table 3. Buffer capacities for unit soil mass and for unit area, by horizon, for the three locations. Soil mass values are from Federer (1983)

				Buffer capacity	
Location	Horizon	Thickness mm	Soil mass Mg ha^{-1}	mmol (H^+) $kg^{-1}pH^{-1}$	mmol (H^+) $ha^{-1}pH^{-1}$
Maine	Oe	50	53	54	2.9
	Oa	90	104	65	6.8
	E	80	943	12	11.3
	Bhs	60	331	14	4.6
	Bs	215	1591	11	17.5
	Total	—	3022	—	43.1
New Hampshire	Oe	30	33	104	3.4
	Oa	60	67	35	2.3
	E	25	314	5	1.6
	Bhs	45	261	12	3.1
	Bs	390	2980	8	23.8
	Total	—	3655	—	34.2
Connecticut	Oe, A1	3	72	21	1.5
	A2	105	995	9	9.0
	Bs1	185	1840	9	16.6
	Bs2	240	2642	10	26.4
	Total	—	5549	—	53.5

For northeastern forest soils our data indicate that organic fraction is an excellent determinant of buffer capacity. General similarity of our data to Bolt's data suggests that soils with similar organic contents may differ only by a factor of two or three in their buffer capacities. The relationship between organic fraction and buffer capacity might be useful for mapping soils sensitive to acid rain. Previous maps by McFee (1980) and Olson et al. (1982) have been based largely on cation exchange capacity, which is more difficult to obtain and probably more variable than the organic fraction. Cation exchange capacity is dominated by organic matter exchange in many northeastern forest soils (Kalisz and Stone 1983), so it is not surprising that buffer capacity also is closely related.

Buffering analysis for acid precipitation studies should be done on a unit-area basis. The annual input of about 1 kmol (H^+) ha^{-1} in northeastern precipitation can be compared with soil buffer capacities of 2 to 10 kmol (H^+) ha^{-1} pH^{-1} in the forest floor and 30 to 40 kmol (H^+) ha^{-1} pH^{-1} in the mineral soil. Using our buffer capacity values with the worst case assumption that there are no mitigating factors, adding all the H^+ in precipitation to the forest floor would produce a pH change of one unit in the floor in only 2 to 10 years. Spreading the H^+ through the whole soil mass would require 30 to 50 years for a change of one pH unit. An important point is that because of their mass, the mineral horizons probably play an important role in buffering H^+ additions.

There is little available information for comparison with our data about how acid rain might affect soil pH. Reuss (1978) and McFee et al. (1977) have estimated changes in soil pH by calculating the potential shift in percent base saturation resulting from annual precipitation of 1000 mm at pH 4.0. They conclude that soil pH may decline between 0.05 and 0.1 unit per decade, or about half the rate we calculated previously.

Our data suggest that the forest soil may not be the super buffer that is sometimes depicted. There is potential for significant changes in pH if precipitation pH continues to average 4.0. An obvious need is more information about mitigating factors. For example, at all of our study sites, the pH of precipitation increases during passage through the canopy. Throughfall often is around pH 5, representing 0.1 kmol (H^+) ha^{-1} yr^{-1}. This much smaller addition apparently would slow the potential rate of change in soil pH, though possibly at the expense of acidification of litterfall.

CONCLUSION

Should forest managers be concerned about the effects of acid rain on forest soils? We believe that our data suggest that the buffer capacity of forest soils from three widely spaced sites in New England is not particularly large, and that significant changes in soil pH possibly could occur over a few decades. The concern that acid precipitation may accelerate soil acidification seems valid. A decline in soil pH could affect such processes as leaching, weathering, cation exchange, and microbial activity, and change the nutrient status. Such changes are likely to be gradual and extremely difficult to detect and quantify.

For the present, forest managers can expect only very general recommendations about how best to protect forests and forest soils against acid rain. Buffer capacity may be a useful tool in developing more specific recommendations, once mitigating factors are more clearly defined.

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DISCUSSION

Question:	Your unit of buffer capacity appears at first to be nonlinear. That is, it will take more hydrogen to change the soil pH from 3 to 2 than from 7 to 6. Could you comment?
Answer:	Certainly, that is what we anticipated. At first, we were surprised to see otherwise, but the literature indicates this to be the case, certainly for buffering determined by adding hydroxyl solutions. I reported here only the 0.1 N additions. We also tried 0.01 N and 1 N. The 1 N drove the pH down below 2 in many cases, and when we plot the buffer capacity it is linear even at those levels. I do not know why that occurs. The literature does not explain it very well, but it does appear to be a linear relationship.
Question:	Could you comment on the implication that in 200 years the pH would be down to zero? Your model indicates this.

Answer: Obviously there are neutralizing factors that we must learn a whole lot about. What we were looking for is an index of what the changes might be. We have not been able to detect changes, to the best of my knowledge, in soil pH very adequately over 20- to 30-year periods. It will be difficult to quantify these pH changes and obviously we have to know more about what neutralizes them.

Question: Can something else, such as volatilization, account for differences in the hydrogen sources and sinks in the model presented?

Answer: Very definitely. The model as it was presented is as it is currently understood for Hubbard Brook. The model is constantly undergoing changes as we learn more about processes and mechanisms. As equipment and methodologies change we shall be able to improve upon the hydrogen ion budget and add additional sources and sinks.

Solubility and Mobility of Aluminum by Acidification of Soils

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ABSTRACT

Soils are complex dynamic systems, which occur in nature as products of processes of soil formation and weathering. Man is an indisputable factor in soil formation, and this role of man has intensified with the development of human society, agriculture and technology. Acid precipitation is one of the many components which have been added to soils by intensified economic activity. Adverse effects of increased acidity have been correlated with the quality of surface waters. No such correlation between the pH of acid precipitation and pH of soils has been established, and such a simple correlation should not be expected. Aluminum is not a major component of acidic precipitation; however, it is generally true that the concentration of Al in soil solution is pH dependent. Aluminum exists in soils in a number of solid and solution forms. The soluble forms of aluminum are controlled by the pH and the anion association. Aluminum hydrolyzes readily, and anions associated with Al have an effect on hydrolysis. The formation of soluble complexes of Al, such as $AlSO_4^+$, influences many reactions. Their potential importance in soils, as it relates to exchange reactions and mobility of cations, has not been recognized.

A comparison of the soil solution chemistry of Al in the presence of Cl^- and SO_4^{2-} ions shows significant differences in the distribution of aluminumion species. In the presence of SO_4^{2-} ions, a substantial amount of aluminum exists as monovalent $AlSO_4^+$, which is not as effective as trivalent aluminum (Al^{3+}) in competing with basic cations for occupying exchange sites. Thus, in SO_4^{2-} systems, a substantial amount of Al is present in a form which can easily move in the soil profile or can leach out of the soil profile to the aquatic environment. The ratio of $(AlSO_4^+)/Al^{3+}$ is controlled by the activity of SO_4^{2-} ions. A 10-fold change in (SO_4^{2-}) results in a 10-fold change in this ratio. On leaching of $AlSO_4^+$ ions from soil systems to aquatic systems, dilution effects would effectively revert the $AlSO_4^+$ ions to Al^{3+} ions.

INTRODUCTION

Aluminum is the most abundant metal element in the Earth's crusts and the aqueous chemistry of aluminum under acidic environment is of great importance: aluminum exists in many different soluble forms, as controlled by the pH, anion association, etc. In fact, reactions between Al^{3+} and OH^- are among the most important inorganic reactions that occur in all, except calcareous, soils. Although similar reactions between the ferric ion and OH^- almost surely exist, they occur at a much lower pH. This is because the bonding energy between Fe^{3+} and OH^- is much greater that that between Al^{3+} and OH^-. However, some of the principles discussed here would also be applicable to other metal elements.

It is safe to say that many areas of the world, especially of industrialized societies, are receiving acid rain. Over the last few decades, the acidity of the rain has been increasing. There has been great pressure in the recent past (especially in North America) to assess and quantify the effects of acidity due to acid rain. This question is not an easy one to answer, because acid rain is not the only source of acidity, especially when one addresses the question as it relates to soils. Soils are complex dynamic systems which occur in nature as products of processes of soil formation and weathering. Every soil passes through a period of development from stable parent rock to develop its own particular soil properties.

The property of a soil is a function of five soil-forming factors—climate, organisms, relief, parent material and time. How does acid rain fit into this equation? Phenomena of atmospheric precipitation are part of climate. It is a primary source of soil moisture, and a number of substances enter the soil by means of atmospheric precipitation, the significance of which cannot be underestimated because of their potential to influence soil formation.

So far, everything seems to be logical and normal, but let us see what man does to this equation. The economic activity of man introduces many interventions in nature, which make this creature indisputably a factor in soil formation and frequently a powerful one. This role has intensified with the development of human society and technology. Acid rain is a component which has been added to soil by the activity of man in industrialized societies. It is in this context that one can discuss how acid precipitation will alter soil constituents and affect those soil properties which are important to the quality of a soil.

Fundamental and well-known chemical cycles show us remarkably well the relationship of emissions of sulfur and nitrogen oxides to soil acidification, hence the need to understand the composition of the soil solution as affected by acid rain. Changes in soil solution chemistry can have major potential impacts on forest productivity as well as on the chemistry and productivity of aquatic systems and fish habitat.

Once rain falls on the ground it can move in the form of overland flow and also through the soil profile by infiltration and percolation: it can thus have an effect on ground-water composition and on changes in the aquatic systems.

There have been established some correlations between the acidity or pH of rain water with that of fresh-water lakes; however, the soil system is too complex for the relationships to be simple ones.

A soil system consists of three states of matter — solid, liquid and gas. The liquid consists of an aqueous solution containing a large number of components. The nature, direction and rate of chemical reactions are determined by the characteristics of reactants and products, their concentrations and amounts, mechanisms of supply and removal from site of action, temperature, pressure, etc. Concentrations of components depend to a considerable extent on reactions involving the products of dissolution of solids, complex formation, exchange between solution and the negative-charge sites solid of surfaces, and on the reactions with water and components of the gas phase. One of the most important of the reactions limiting the concentrations of the various components in solution is the precipitation and dissolution of sparingly soluble solids. These include aluminum compounds.

Aluminum exists in soils in a number of forms. For the sake of convenience two groups can be recognized:

(a) aluminum forming a structural part of the clay minerals,
(b) aluminum not part of the clay minerals, which may be referred to as free aluminum, consisting of:
    (i) cations in solution and exchangeable cations,
    (ii) solids, both amorphous and crystalline.

Group (a) is formed during weathering when aluminum is released from primary minerals and is precipitated as secondary minerals, largely as alumino-silicates.

The question may be asked: What is the origin of this free aluminum? It is this question that is relevant to the increased acidity received in rain water. When the negative exchange sites on a clay are saturated with H^+ ions, the surfaces of the clay are in a very acid medium. This leads to the dissolution of Al from the clay.

We may now consider the aluminum equilibria, for these serve as an example of simultaneous equilibria in natural soil systems. Soil solution Al^{3+} is in equilibrium simultaneously with $Al(OH)_3(s)$, $Al(OH)_{3-x}\ SO_{4x/2}(s)$, soil solution $AlSO_4^+$, $Al(OH)_2^+$ and $Al_6(OH)_{15}^{3+}$ and exchangeable Al. The equilibria are, of course, affected by the activities of other electrolytes and ions. The presence or absence of a particular species of hydroxy-aluminum or trivalent aluminum depends on certain characteristics of the soil (pH is one such characteristic) or, conversely, the presence of a particular species imposes certain characteristics on a soil.

Once this process of dissolution starts and soluble Al appears in the soil solution a multiple number of reactions can occur. Due to the cyclical nature of the environment, such as warming, cooling, wetting and drying, a number of products can be formed. One such product is the formation and presence of aluminum-hydroxy interlayers in clay minerals. Such non-exchangeable Al can reduce the exchange capacity to such an extent that a danger of Ca deficiency for nutritional purposes could result, even though the available exchange sites were essentially saturated with Ca.

Another feature of the non-exchangeable hydroxy-aluminum is that it may be a sink for large amounts of applied phosphate fertilizers and other plant nutrient ions.

The optimum conditions for the formation of interlayers are:

(i) moderate active weathering,
(ii) availability of Al,
(iii) pH = 5.0,
(iv) low organic matter, and
(v) wetting and drying.

The chemical characteristics of aluminum-saturated and aluminum-interlayered Wyoming bentonite show that once the exchange capacity of clay is blocked by the interlayering material, such a change may be irreversible under ordinary circumstances.

The cation exchange capacity of aluminum-saturated bentonite was 79.7 meq $100g^{-1}$ clay and it remained so even after two years of equilibration. However, in the aluminum- interlayered Wyoming bentonite samples, the cation exchange capacity of the samples was drastically reduced from about 80 meq $100g^{-1}$ to 30 meq $100g^{-1}$ and there was no change in this value even after more than two years of equilibration. The ion activity-product $(Al)(OH)^3$ was $10^{-33.10}$.

It must be mentioned that the amount of aluminum precipitated per unit of clay was important in determining both the stability of interlayered aluminum and the permanency of the reduced cation exchange capacity. In the case of Wyoming bentonite, when the amount of aluminum was 8 meq g^{-1} clay, the decrease in cation exchange capacity seemed to be of a permanent nature. When the amount of aluminum exceeded 8 meq g^{-1} clay and approached 16 meq g^{-1} clay, a crystalline phase of gibbsite was formed.

It is concluded from the above discussion that an increase in H^+ ion concentration in the soil, irrespective of source, leads to a gradual destruction of the mineral fraction, with a resultant increase in aluminum and other metal ions (Fe, Mn), together with their corresponding hydroxy compounds these may exist independently or in association with the clay minerals.

The above summarizes the effect of H^+ ions on the release of aluminum. SO_4^{2-} ions are an important constituent of acid rain, and SO_4^{2-} forms ion pairs with many different cations. The importance of such ion complexes can be readily seen from their equilibrium reactions. For example, when the activity of SO_4^{2-} ions is $10^{-3.20}$ mol L^{-1}, the ratio of $AlSO_4^+/Al^{3+}$ is 1. A 10-fold change in the activity of $SO_4(SO_4^{2-})$ results in a 10-fold change in this ratio.

Another cation of interest in acidic soils is Ca, because most of the aluminum saturation of exchange sites occurs at the cost of Ca being replaced.

Somewhat detailed calculations may be made to show:

(i) the distribution of divalent Ca^{2+} and SO_4^{2-} and neutral soluble $CaSO_4^0$,

(ii) correct activities of divalent Ca^{2+} and SO_4^{2-} (which are derived after correcting for complexing in the calculation of ion strength and activity coefficients),

(iii) the activities of Ca^{2+} and SO_4^{2-} when corrections are not made for ion pair formation in the calculation of ion strength.

This shows a difference of 25 to 30%, which is significant.

We may now consider the role of Cl^- and SO_4^{2-} ions, as they influence the soil solution chemistry of aluminum and calcium, pH, exchange characteristics and the solubility ion activity product, $(Al)(OH)^3$, in some acid soils of Canada. The pH of soil suspensions in $CaSO_4$ solution is higher compared to the pH measured in $CaCl_2$ solutions. The reduction of H^+ ions due to SO_4^{2-} was proportional to the H^+ ion activity of the soil suspensions: that is, the greater the activity of H^+ ions (lower pH), the greater the decrease in H^+ ions. This indicates that SO_4^{2-} ions were more reactive at lower pH in increasing the pH of soil suspensions.

Aluminum and hydroxy-aluminum species are the most important constituents which determine "acid strength" in most acid soils. It may be concluded, therefore, that SO_4^{2-} ions in acid soils react in some manner which results in a higher pH in the presence of SO_4^{2-} ions, as compared to pH measured in the presence of Cl^- ions.

I do not want to give the impression that because the presence of SO_4^{2-} in acid rain raises the pH of acid soils it would have a beneficial effect. It must be stressed that there is much more to soil acidity than changes in soil pH.

Some probable mechanisms are:

$$Al^{3+} + SO_4^{2-} \rightleftharpoons AlSO_4^{+}$$

$$Al_n(OH)^{3n-m} + xSO_4^{2-} \rightleftharpoons Al_n(OH)_{m-2x}(SO_4)^{3n-m} + 2\,x\,OH^-$$

$$Al(OH)_3^0 + SO_4^{2-} \rightleftharpoons [Al(OH)_{3-2x}(SO_4)]^0 + 2x\,OH^-$$

The first two reactions are solution-phase reactions and the third is a solid-phase reaction. The first reaction changes the ionic form of aluminum, from trivalent Al^{3+} to monovalent $AlSO_4^+$. This effectively reduces the quantity of Al^{3+} available for hydrolysis with the resulting release of H^+ ions the soil solution. It also reduces H^+ ions taking part in the cation exchange reactions in soils. The exact nature and probability of the second reaction are not known however, this type of reaction could release OH^- ions. The third reaction is the adsorption of SO_4^{2-} ions by amorphous aluminum hydroxide solid phase.

There is some impression from the literature that this mechanism of sulfate adsorption can prevent leaching of cations. This has been related to the mobility of the associated anion and the requirement for a charge balance in the soil solution that would preclude the leaching of cations without their being associated with mobile anions. This concept is attributed to Johnson and co-workers. Wiklander (1980) has also attributed the increased retention and reduced leaching of salt cations in the presence of polyvalent cations, especially with phosphate anions, to the increased cation exchange capacity rather than to so-called charge balance. These authors seem to ignore the ion association concept. The presence of SO_4^{2-} ions leads to the formation of many complexes; moreover, the electrical neutrality must be maintained, so leaching will be increased.

The significance of the presence of sulfate ions on the ionic distribution of aluminum species may be demonstrated as follows. In the chloride system, which does not form complexes with Al, the aluminum will exist as trivalent aluminum (Al^{3+}) and divalent $AlOH^{2+}$. The ratio of Al^{3+} to $AlOH^{2+}$ is controlled by the pH of the system. In the presence of SO_4^{2-} ions aluminum will exist as trivalent Al^{3+}, divalent $AlOH^{2+}$ and monovalent $AlSO_4^+$. In the Cl system, 93% of aluminum is present as trivalent aluminum (Al^{3+}), as compared to only 35% in the presence of SO_4^{2-} ions. As much as 60% of aluminum is found to be present as monovalent $AlSO_4^+$, a complexed ion species of aluminum. Trivalent cations are much more effective in influencing the exchange reactions than monovalent cations, and thus a substantial amount of Al present in the monovalent form could move in the soil profile or could leach out of the soil profile into ground-water.

As mentioned earlier, the ratio of $AlSO_4^+/Al^{3+}$ is determined by the concentration of SO_4^{2-} ions. If the concentration of SO_4^{2-} increases, the amount of $AlSO_4^+$ also increases, and on dilution the proportion of trivalent aluminum (Al^{3+}) increases. This is of great importance to the aquatic system, because through the dilution effect any monovalent $AlSO_4^+$ entering the lake system would revert to Al^{3+} ions, and this is of significance when the toxicity effects of aluminum are being considered.

We may next consider the ionic activity product of the solid phase of the aluminum-hydroxy complex. In spite of the fact that the pH is higher in SO_4^{2-} systems, the aluminum hydroxy sulfate compound formed is much more soluble and, therefore, mobile.

There is a great interest in determining the effect of aluminum on the quality and productivity of different plants. It has been shown that aluminum exists in different forms. The question may be asked: are all the species and forms of aluminum as they exist in soil solution equally toxic? This is a difficult question to answer because, in spite of the tremendous amount of work carried out on aluminum, our knowledge is still very limited on the exact nature of aluminum-hydroxy complexes and their effects on plants. Recent work of Pavan, Bingham and Pratt (1982) has considered this aspect, and their conclusions are:

(1) the gypsum treatment to acid soil causes a significant amount of Al^{3+} to ion pair with SO_4^{2-} to form $AlSO_4^+$, which accounts for 36 to 43% of Al_t present in the soil solution,

(2) sulfate also forms an ion pair with Ca, and approximately 30% of total Ca (Ca_t) present in solution of the gypsum-treated soil exists as the $CaSO_4^0$ species.

(3) although the gypsum treatment increases the Al_t concentration in soil solution, the change in leaf Al is not pronounced. This lack of Al uptake, as judged by leaf Al values, may be a reflection of the formation of a less available Al species — $AlSO_4^+$.

The correlation coefficients between the relative root growth (growth expressed relative to the growth of plants receiving twice the lime equivalent treatment) and various Al parameters have been calculated as:

(1) percent base saturation ($r = -0.81$),
(2) concentration of Al_t ($r = -0.82$),
(3) concentration of Al^{3+} ($r = -0.92$),
(4) activity of Al^{3+} ($r = -0.97$).

These data show that for coffee plants root growth is inhibited progressively by increasing Al levels. Furthermore, they show that the reduction in root-growth correlates best with the activity of Al^{3+}, rather than with other aluminum parameters. These results demonstrate the need for careful planning in order to evaluate the effects of aluminum levels on the germination of seeds, plant growth, etc., which are now receiving great emphasis by researchers and administrators.

The question may be asked: what is a suitable pH to counterbalance the effect of acidity? The answer to this question involves soil conditions where the release of Al from clays is prevented. In general, low pHs are associated with low degrees of base saturation. Provided a sufficient number of soils is investigated, it is always possible to show a positive correlation between the two. However, the correlation is not precise enough to be of much practical value for individual cases.

Schofield (1952) introduced the concept of lime potential, pH-1/2 p (Ca + Mg), which takes into account the concentrations in solution of the major cations, Ca and Mg, in soils. This ratio governs or is governed by the same ratio of exchangeable Ca^{2+} + Mg^{2+} to exchangeable H^+. It is thus a measure of the degree of base saturation, provided that exchangeable Al can be ignored, i.e., for soils that are not strongly acidic. Since we are dealing with soils where exchangeable Al^{3+} cannot be ignored, because appreciable quantities are present, it is necessary to find some other property of the soil solution.

Turner and co-workers added an extension to the lime potential equation of Schofield and called it the corrected lime potential $(CLP)_g$, where 'g' relates to gibbsite. The $(CLP)_g$ can be expressed in the form:

$$pH-1/2\,p\,(Ca + Mg) + 1/3\,(py-34.0)$$

where 'y' is the ion activity product of $(Al)(OH)_3$ for the particular soil under investigation. A plot may be shown of $(CLP)_g$ versus degree of base saturation. It implies that if exchangeable Al^{3+} is absent, then the soil is base saturated. In other words, exchangeable H^+ does not exist in soils. Although it is not true that exchangeable H^+ does not exist in soils, it can be shown that it can never be more than a very small fraction of the total exchangeable bases. When the $(CLP)_g$ is less than 3.8 the soil contains exchangeable aluminum (Al^{3+}) and such soils require lime to neutralize the exchangeable Al^{3+} present, thereby removing the probability of aluminum toxicity.

However, for long-term plant productivity and the maintenance of soil nutrient status, the object is to follow liming practices that will ensure that the soil as a medium for growing crops is not impaired. In other words, the productive capacity of the soil is maintained or improved regardless of how long cropping or harvesting is continued.

The Nature, Forms and Transformations of Sulphur in Soils

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ABSTRACT

The importance of sulphur (S) as an atmospheric pollutant and as an essential nutrient and the increasing occurrence of S deficiency around the world have emphasized the need to obtain an understanding of the nature, forms, and transformations of S in soils. In particular, although, most soil S exists in combination with organic matter, the biological availability of such S has only been quantified in a few areas and very rarely in soils receiving significant amounts of exogenous inorganic sulphate. Many researchers have measured the different capacities of forested and agricultural soils to adsorb sulphate. However, there have been only a few measurements of the incorporation of sulphate into organic matter, although this undoubtedly occurs. Development of new techniques of measuring microbial biomass and S content, in conjunction with isotopic techniques, permits the determination of the nature and dynamics of microbial S. Together with laboratory incubation studies designed to investigate processes involved in S transformations, and observations of S content of organic matter in relation to carbon (C) and nitrogen (N) across environmental gradients and cultivation chronosequences, the new techniques have yielded the framework for the construction of a conceptual S cycle and predictive computer models in soils developed under grasslands. Preliminary evidence from forested soils suggests that the same processes and hypotheses apply to forest ecosystems, but that the rate of cycling is different because of abiotic differences and the different nature and deposition of the C inputs into the soil. This paper reviews some of the process studies that have helped to elucidate the S cycle dynamics and discusses the possibility and probability of similar processes being active in forest soils.

INTRODUCTION

During the last decade the importance of sulphur (S) as an atmospheric pollutant and as an essential nutrient and the increasing occurrence of S deficiency around the world have emphasized the need to obtain an understanding of the nature, forms, and transformations of S in soils. In particular, although in general most soil S exists in combination with organic matter, the biological availability of this S has only been quantified in a few areas (Freney and Williams 1983) and very rarely in soils receiving significant amounts of exogenous inorganic sulphate. The ability of various forests and agricultural soils to adsorb sulphate has been documented, but, to date, there have been only a few measurements of the incorporation of sulphate into organic matter, although this undoubtedly occurs.

In North America, S deposition values range widely, with most areas receiving between 5 and 40 kg SO_4^{2-} ha^{-1} yr^{-1} (Gibson and Linthurst 1982). It is generally recognized that water bodies receiving more than 20 kg SO_4^{2-} ha^{-1} yr^{-1} are thought to be degrading. However, information on acid forest soils is sparse and difficult to interpret because of differences in soil type, climate, and vegetation.

In many forest ecosystems the quantity of S deposited is greater than that leaving the soil. For instance, at the Coweeta Hydrological Station in North Carolina, Swank and Douglas (1975) estimated the net retention of S to range from 6.2 to 13.2 kg SO_4^{2-} ha^{-1} yr^{-1}. This extra S entering the system could be retained by (a) reacting with soil colloidal particles by means of an adsorption process on aluminum sesquioxides or hydroxy polymers, or (b) immobilization and retention as part of the soil organic matter. Recent work (Fitzgerald et al. 1982; David et al. 1982) has emphasized that the latter process does occur. Data for forest soils (David et al. 1982) clearly show that the total amount of soil S varies with soil depth and is related to the quantity of soil organic matter. Data from both coniferous and hardwood sites show the same type of distribution with profile depth. Inorganic S forms accounted for less than 20% of the total S in any horizon; in most of the A, B, and C horizons, the greatest amount of S in the inorganic form occurs as the sulphate anion. Organic S, generally 80 to 90% of the total S with depth, has been identified as both carbon-bonded S and ester-bonded S; in general, ester-bonded S is less than 30% of the total organic S. This contrasts with data taken from cultivated soils derived from grassland, where ester-bonded S accounted for 50% of the total organic S. In deciduous woodland it has been shown to average 35% (Bettany et al. 1973).

The main point to be emphasized is that organic S is not inert. In many S-deficient areas of the world, the availability of S to plants depends on net S mineralization from organic S forms. Most of the information accruing on organic S in soils comes from areas such as former grasslands in Australia or western Canada where the rate of mineralization of organic S has been an important factor in understanding the S availability in soils. In the Canadian prairies, for example, S deficiency increases with time of cultivation. It is forecast that N and S will be the two most prevalent nutrient deficiencies in such soils (Bettany et al. 1983).

This paper reviews information on S transformation processes and relates these processes to changes that could occur with the addition of extra S in acid rain.

FORMS SOIL S

Total S data are of little use in providing interpretive criteria for the soil S cycle other than as a broad indication of pollution. However, the relationship of S to C and N in soil organic matter gives a general outline of the processes of humus formation and transformation occurring within the soil profile (Bettany et al. 1973, 1979). Marked variation in C:N:S ratios can be observed because of the interaction of soil-forming factors, such as parent material, climate, vegetation, and cultivation (Table 1). The significance of these variables may relate to the available S levels in soils because wide ratios often coincide with low amounts of net mineralization and decreased S supply (Bettany et al. 1974, 1979; Barrow 1961; Kowalenko and Lowe 1975b).

Organic S

Current analytical techniques permit only a broad fractionation of organic S compounds in soils. Two principal groups have been identified: one in which S is directly bonded to carbon (C-bonded S), and another in which S is linked to carbon through an O or N atom (organic sulphates). The former group includes free or combined S amino acids and sulphonates, and the latter the sulphate esters, thioglucosides and sulphamates. Problems with the analytical determination of these fractions have been discussed elsewhere (Freney et al. 1970, 1972). Most workers determine organic sulphate by reduction with hydriodic acid (HI reducible S); C-bonded S is then calculated as the difference between total S and HI-reducible S. It is obvious that this methodology is subject to error and lacks "biological significance". However, the fractionation does take on meaning when considered in terms of the soil-forming factors and available S (Bettany et al. 1973, 1979, 1980).

Generally, the HI-reducible S fraction is considered more biologically active or "labile", and accounts for 27 to 78% of the total S in surface soils with a mean value of approximately 50% (Bettany and Stewart 1983). The percentage of HI-reducible S shows considerable variation across environmental gradients and cultivation chronosequences; it generally increases with depth in the soil profile and is concentrated in the clay and fulvic acid fractions of soils.

Table 1. Carbon, nitrogen and sulphur ratios of world soil types

(a) Effect of parent material

Country	Parent material	C:N:S	C:N
Scotland	Granite	117:6.1:1	16.9
	Slate	104:7.0:1	14.8
	Basic igneous	102:7.3:1	14.0
	Old red stone	95:7.3:1	13.0
	Calcareous	89:7.9:1	11.3

(b) Effect of weathering

Country	Weathering stage	C:N:S	C:N
New Zealand	Weakly weathered	156:9.1:1	17.2
	Moderately weathered	150:8.3:1	18.0
	Strongly weathered	158:7.7:1	20.6

(c) Effect of climate and cultivation

Country	Soil type	C:N:S	C:N
	Virgin soils		
Canada (western)	Brown Chernozems	85:7.1:1	12.0
	Black Chernozems	96:7.7:1	12.5
	Gray Wooded	271:12.5:1	21.7
	Gleysols	78:5.0:1	15.6
	Cultivated soils		
Canada (western)	Brown Chernozems	58:6.4:1	9.1
	Dark Brown Chernozems	63:6.9:1	9.1
	Black Chernozems	83:7.6:1	10.9
	Gray Black Transitional	100:8.1:1	12.3
	Gray Wooded	129:10.6:1	12.2
USA	Brown Chernozems	74:6.5:1	11.4
	Black Chernozems	73:6.1:1	11.9
	Podzols	108:8.2:1	13.2
	Podzols	141:9.3:1	15.2
	Podzols	139:13.2:1	10.6

Table 1. *Carbon, nitrogen and sulphur ratios of world soil types (continued)*

(c) Effect of climate and cultivation

Country	Description	C:N:S	C:N
Australia	Acid soils	126:8.3:1	15.2
	Alkaline soils	92:6.6:1	14.0
India	Hill	113:14.5:1	7.8
	Tarai	164:17.9:1	9.2
	Lateritic	59:5.5:1	10.7
	Alluvial	74:7.4:1	10.0
	Coastal saline	129:12.8:1	10.1
East Africa	Forest	146:15.9:1	9.2
West Indies	Regosol	155:10.1:1	15.4
	Regosol	111:7.0:1	15.8
	Ultisol	107:9.2:1	11.7
	Mollisol	97:8.1:1	12.0
	Inceptisol	133:11.0:1	12.1
	Inceptisol	85:9.7:1	8.8
	Inceptisol	96:8.9:1	10.8

The C-bonded S fraction contains both the labile S amino acids, protein S, and the more resistant sulphones, sulphonic acids, and heterocyclic compounds. It is likely that a portion of this fraction is highly labile because experiments using tracers show that recently immobilized sulphate is re-mineralized from both HI-reducible and C-bonded fractions (Freney et al. 1971; Maynard 1983).

The soil organic fraction comprises a complex heterogeneous mixture of soil organisms, and partially decomposed and transformed plant, animal, and microbial residues, in intimate association with the soil minerals. It is, therefore, not surprising that determination of the two S fractions on whole soils gives little information on the turnover dynamics of S in organic matter. Attempts have been made to fractionate the soil organic matter before analysis for S forms to obtain more meaningful results. The various approaches that have been taken include:

1) Isolation, identification, and determination of individual compounds belonging to definite chemical groups
2) Chemical extraction followed by physicochemical separations of various fractions, such as humic and fulvic acids and humin
3) Physical separation of soils into various organo-mineral size fractions
4) Biological techniques, aided by radio-and stable isotopes, with the objective of isolating and identifying fractions significant in terms of nutrient cycling.

The first two approaches have been tried by numerous workers for over half a century. "Free" individual chemical compounds extracted from soils account for only a minor percentage of the total organic matter present. Extraction of soils with strong acid or alkali solutions produces fractions which are complex mixtures of hydrolysis products and soluble humus. Although some progress has been made in the identification of functional groups and molecular properties of organic matter (Schnitzer 1978), the artifacts produced by extraction and the universal applicability of such procedures have been open to question (Kowelenko 1978).

It is accepted that recent techniques cannot avoid artifact formation during chemical extraction and purification of organic matter fractions, but it can be minimized. For example, the physical separation of whole soils into organo-mineral complexes of various particle sizes by dispersion (usually with ultrasonic energy), followed by densimetric separation or centrifugation, yields fractions which have minimal chemical alteration. Such a procedure enables the study of the role of inorganic constituents in the stabilization and transformation of humus (Anderson et al. 1981; Turchenek and Oades 1979). Distinct differences in the forms and distribution of organic N and S among particle size fractions have been observed, suggesting that S follows different pathways in humus formation and transformation than do C and N. In two Canadian prairie soils, S, in contrast to C and N, was found to be more concentrated in the fine-clay fraction, and most of this S was HI- reducible (Anderson et al. 1981). Both the C:S and N:S ratios decrease in the smaller particle size fractions, and it was proposed that the clay-associated humus acts as a medium-term storehouse for available S. Changes in the C:N:S ratios of soil clays and the determination of HI-reducible S in this fraction offer promise as an index of soil organic matter quality, so that changes in soils caused by cultivation and erosion can be monitored.

Consideration of the biologically significant fractions of soil organic matter inevitably involves the role of the soil biomass. Complete understanding of the S cycle requires an understanding of the forms of S in soil microorganisms and of the mechanisms involved in microbial transformations. Methodology for the determination of biomass S in soils has just become available (Saggar et al. 1981a), and experimentation is currently under way to study the forms of S in microbes and their role in S cycling. Early results show that only 2-3% of the total S in soils is contained in the microbial biomass. The main portion of S in bacteria appears to be in the form of amino acids, with about 10% as HI-reducible S (Saggar et al. 1981a). Reports of S compounds other than amino acids and related compounds are rare, although small amounts of organic sulphates (choline sulphate) have been found in bacterial cell walls (Fitzgerald and Luschinski 1977), and a bacterial sulpholipid has also been identified (Goren 1970, 1971). Like bacteria, the main portion of S in fungi is in amino acid form. However, fungi have a larger portion of organic sulphates, such as choline sulphate. Fungi appear able to store S as choline sulphate when S is in adequate supply (McGuire and Marzluf 1974; Scott and Spencer 1968). Recent experiments show that the percentage of total S as HI-reducible S increases significantly with increasing concentrations of sulphate in the growing medium (Saggar et al. 1981a). There is also evidence that significant amounts of various arylsulphates may be present in fungi (Burns and Wynn 1975), and elemental S is contained in some species (Pezet and Plant 1977).

TRANSFORMATIONS OF S IN SOILS

The transformation of S in soils is considered to be mainly microbial (Freney et al. 1971), although some strictly chemical processes (for example, the oxidation of iron sulphide) are also possible (Bloomfield and Coulter 1973). There are four distinct microbial processes:

1) Mineralization: a process in which large organic molecules containing S are broken down to smaller units and eventually to inorganic sulphate
2) Immobilization: simple inorganic S molecules (mainly sulphate) are converted to organic compounds
3) Oxidation: inorganic S of lower oxidation states (elemental S, thiosulphate, polythionate, sulphides, etc.) are generally converted to sulphate as a stable end product
4) Reduction: sulphate and other partially reduced S anions are converted to sulphide.

Although there are organisms capable of performing all these processes in all soils, mineralization and immobilization are the dominant transformations that occur in well-aerated arable soils of the world.

Mineralization

The mechanisms involved in the mineralization of organic S are still largely unknown. It is believed that during the breakdown of organic substrates by heterotrophic microorganisms, part of the S is retained for cellular metabolism, and only excess amounts are released to the soil "available pool" as inorganic sulphate.

It was originally thought that as S and N are closely related in soil organic matter, these two elements would mineralize in related amounts. However, numerous experiments show that this is not the case, and considerable controversy exists in this area. In some studies, incubation of soil samples in the laboratory showed that mineralization of S occurred concurrently with N at ratios wider than that of the soil organic matter (Bettany and Stewart 1983), although in other studies narrower ratios were observed. An even greater contradiction is shown from other studies, where mineralization of N occurred with concomitant net immobilization of S (Saggar et al. 1981b).

A recent review (McGill and Cole 1981) has given a possible explanation for the observed behavior of S in the mineralization processes. These authors suggest that if any element is associated with soil organic matter for which there are specific degradation mechanisms, it may be mineralized independently of other elements. For example, the existence of sulphohydrolase enzyme activity has been demonstrated in soils (Fitzgerald 1976; Tabatabai and Bremner 1970a, 1970b). Such enzymes are highly specific and release inorganic sulphate through hydrolysis of organic sulphates. This type of mineralization is called "biochemical mineralization" and results from a specific need for S. In contrast, "biological mineralization" of both N and S bonded to C occurs as a result of microbes utilizing the C energy source, and not specifically in response to a need for N or S. The net mineralization of S is then the result of the combination of the two mechanisms.

A further note of some importance comes from studies of laboratory incubation techniques used to determine net mineralization rates. Incubation of western Canadian surface soils in a closed system has shown a net immobilization of S with concurrent mineralization of N. Incubation of the same soils in an open system, in which the mineralized N and S were removed by leaching with nutrient solution, has shown net mineralization of both S and N. The amounts of N released by both incubation techniques were found to be the same (Maynard et al. 1983). These results suggest the existence of an inhibitor feedback to S mineralization, possibly through deactivation production limitation of enzymes such as sulphatases involved in biochemical mineralization.

The factors that affect the rates of S mineralization are numerous. Environmental conditions that influence microbial growth and the production and activity of enzymes, such as moisture, temperature, pH, and availability of substrate, have the most significant effects. However, other factors such as the presence of plants (Freney and Spencer 1960; Maynard 1983) and drying and heating enhance the release of inorganic sulphate from soil organic matter (Freney 1958, 1967; Kowalenko and Lowe 1975a).

Immobilization

The transformation of inorganic sulphate to organic S compounds in cellular material is termed "assimilatory sulphate reduction". The process is possible in microorganisms and plants but not in animals. A more complete discussion of the pathways and mechanisms involved is given elsewhere (Freney 1967; Postgate 1968; Roy and Trudinger 1970).

The mechanisms of the breakdown of plant, animal, and microbial compounds and their subsequent incorporation into the soil organic matter are largely unknown. Experimentation in this field of study is still at an elementary level and has centered on the fate of labeled compounds and plant material during incubation. An early study showed that little incorporation into soil humic acid occurred when sulphate and amino acid S were added directly to soil. However, when rye plants were grown with labeled $^{35}S\text{-}SO_4^{2-}$ and the residues incorporated into soil, appreciable amounts of the labeled S were found in the soil humic acids (Scharpenseel and Krause 1963). Another study showed that after 168 days of incubation about 50% of a labeled sulphate was incorporated into the soil organic fraction. The addition of a C substrate (glucose) increased the amount incorporated to 82%. The radioactive label was found in both HI-reducible and C-bonded S fractions, with the HI-reducible fraction exhibiting greater specific activity. The study further showed that the fulvic acid fraction contained about 75% of the immobilized S, of which approximately 90% was in the HI-reducible form (Freney et al. 1971).

A recent, short-term (64-day) incubation study has confirmed that inorganic sulphate, when immobilized, finds its way mostly into the fulvic acid fraction of soil (Saggar et al. 1981b). The fulvic acid fraction was obtained as the acid-soluble fraction following extraction of soils with a mixture of 0.1 M NaOH - $Na_4P_2O_7$. It was hypothesized that the fulvic acid fraction is a highly active component of soils represented by low molecular weight humic materials, cellular metabolites, and relatively simple decomposition products of plant, microbial, and animal origin. A long-term incubation test by the same workers showed a progressive transformation of the immobilized S into the more resistant humic acids and humin fractions. Similarly, in forest soils, Fitzgerald et al. (1982) found that part of added $^{35}SO_4^{2-}$ was rapidly converted to nonextractable ester sulphate and carbon-bonded S forms.

Oxidation

The oxidation process is of considerable importance because the ultimate source of S in soils is the S-bearing minerals, and many S fertilizers are based on reduced forms of S. Elemental S, sulphide, and thiosulphate can be oxidized slowly in soils by purely chemical means; but the microbiological oxidation by a diverse group of autotrophic, photosynthetic, and heterotrophic bacteria, fungi, and actinomycetes is much more rapid under favorable conditions (Wainwright 1978; Ralph 1979). The oxidation of sulphide minerals in soils is more complex than oxidation of elemental S and appears to involve both chemical and microbiological reactions (Freney and Williams 1983; Ralph 1979).

The large number of environmental and microbiological factors influencing S oxidation introduces considerable variability in oxidation rates among soils. In a study of 273 Australian soils, 19% showed no appreciable oxidation of added elemental S, while 39% showed very rapid oxidation rates (Vitolins and Swaby 1969). Soils from the northern U.S. and western Canada also showed a wide variability in S oxidation rates (Attoe and Olson 1970; Janzen et al. 1982).

Reduction

Dissimilatory or "respiratory" sulphate reduction is brought about exclusively by certain bacteria, which use sulphate as the terminal electron acceptor for their respiratory processes. The predominant microorganisms involved in this reaction are obligate anaerobes belonging to two groups of bacteria, ***Desulphotomaculum*** and ***Desulfovibrio***. The reduction of sulphate to sulphide only occurs in environments where air is absent. As a result, the process is not common in normal well-aerated agricultural soils. However, in soils which are subject to periodic flooding or waterlogging, conditions can exist for the production of large amounts of H_2S, especially where significant quantities of readily decomposable plant residues are present (Bloomfield 1969; Connell and Patrick 1968).

The production rate of H_2S in tidal marsh soils can be very high. Studies of Georgia marshland soils showed that for the topmost 35 cm of soil, as much as 201 mmol sulphide $m^{-2}\,day^{-1}$ were produced (Skyring et al. 1978). Such a large production rate needed a large proportion of the organic carbon produced by the *Spartina* vegetation. It is likely that such anaerobic processes in marshlands contribute significantly to the cycling processes of elements in the biosphere.

S CYCLES

A knowledge of the forms and transformations of soil S allows the combination of hypotheses into a cycle and eventually a model to describe the systems. This is a useful exercise from several standpoints. First, it encourages the integration of research work and shows how a specific study fits into the overall scheme of things. Secondly, it encourages better research planning and identifies "missing links" that are often not obvious to workers in narrow areas of specialization. Lastly, and no less importantly, it provides a common ground for discourse among the various disciplines with a resulting product of wide scientific appeal.

The ultimate goal of any cycling study is to resolve a system to a level where accurate predictions can be made. The benefits from such an achievement are many, often involving society and the economy in general. For example, if the effects of pollution (such as acid rain) can be predicted before the damage is observed, various remedial actions can be taken at an early stage. Similarly, if nutrient deficiencies and deterioration of soil quality due to specific management practices can be predicted, programs can be brought into effect to reverse the trend at a minimum cost.

The following conceptual flow diagram describes the main forms and transformations and sets the boundaries of the cycle (i.e., in the soil-plant system under study (Figure 1), atmospheric and groundwater processes are not documented except for the net inflow and outflow of various S compounds at the soil-air and soil-water interfaces). Processes involved have to be incorporated into a descriptive diagram that includes the known biological, chemical, and physical processes, even though methodology may not have been developed to quantify either the size of the nutrient pools or the rates of transfer among them. In this diagram, both soil inorganic and organic S are divided into labile and stable forms (including clay protected, organic forms), and the different chemical nature of S in organic and inorganic soil phases is recognized. Transfers resulting from the uptake of sulphate by microbial biomass are central to the redistribution of different forms of S in soils. The diagram is a concept or hypothesis of the known types of transfers that take place and does not attempt to show the quantities or dynamics involved.

For example, transformations of deposited S in acid rain may take a variety of paths (Figure 1), and it is important to assess each possibility carefully to document the extent of, and competition between, each pathway at each site.

IMPACT OF SULPHATE DEPOSITION IN ACID RAIN ON FOREST SOILS

Sulphate entering a forest ecosystem could theoretically be (a) leached in groundwater, (b) volatilized as mercaptans or H_2S, (c) precipitated as insoluble sulphides, (d) adsorbed into colloidal surfaces or occluded through reaction with aluminum polymeric compounds, (e) precipitated as a salt, for example, $CaSO_4$, (f) taken up by plant roots, or (g) taken up by microorganisms and transformed into organic matter.

Many of these possible mechanisms have been thoroughly researched, and rates could be assigned to specific soil and site characteristics. However, very little work has been carried out on the microbial transformations of S into organic matter, or on factors affecting the immobilization and mineralization of organic S. Immobilization rates are dependent on both C turnover and level of sulphate in solution. The rate of microbial turnover could be decreased as the soil becomes more acid and, also, as a result of change in litter quality. Also, as the soil becomes more acid, increased adsorption of solution sulphate by inorganic colloids could result, thereby decreasing the quantity in solution.

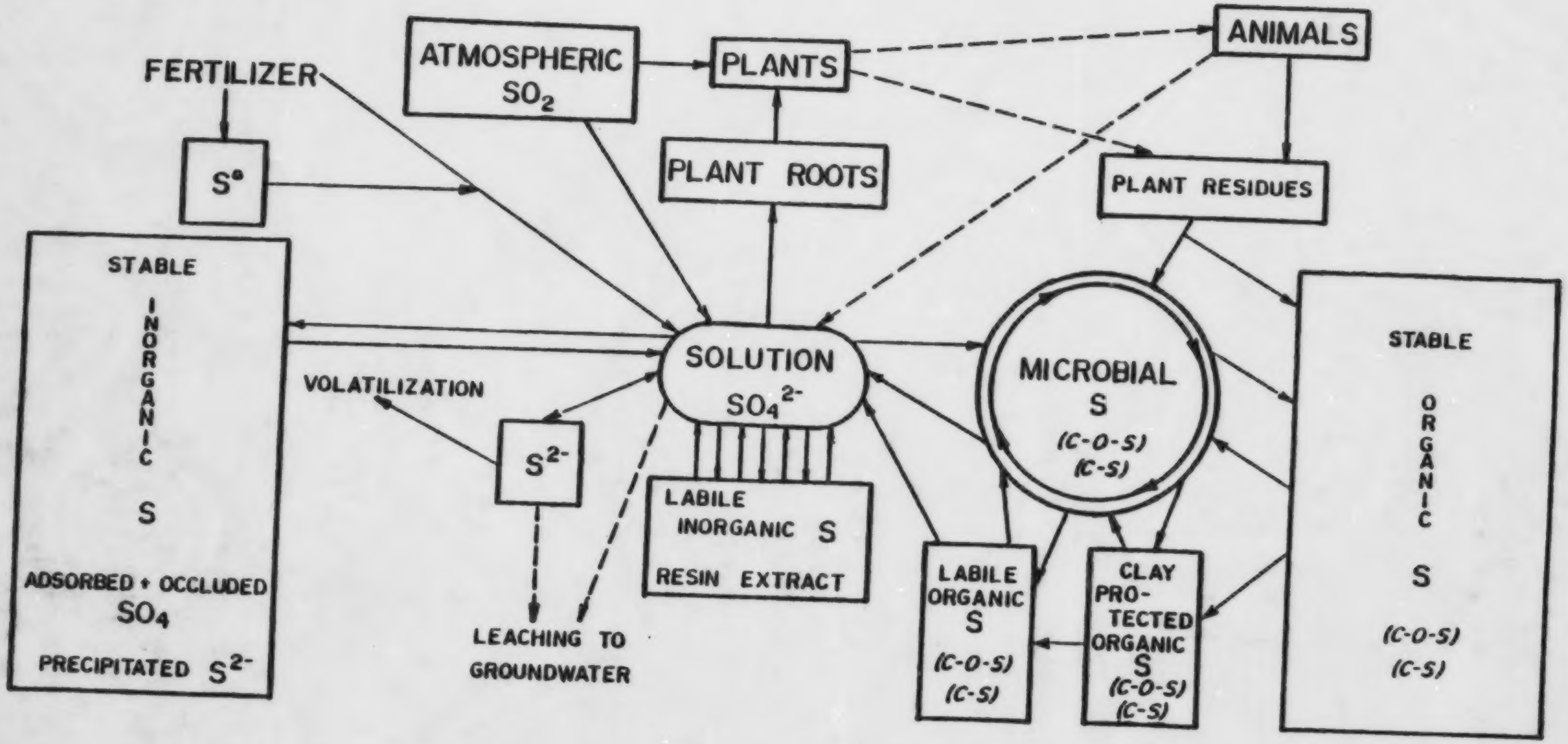
FERTILIZER
S°
ATMOSPHERIC SO$_2$
PLANTS
PLANT ROOTS
ANIMALS
PLANT RESIDUES
STABLE INORGANIC S
ADSORBED + OCCLUDED SO$_4$
PRECIPITATED S^{2-}
VOLATILIZATION
S^{2-}
SOLUTION SO$_4^{2-}$
LABILE INORGANIC S
RESIN EXTRACT
LEACHING TO GROUNDWATER
MICROBIAL S (C-O-S) (C-S)
LABILE ORGANIC S (C-O-S) (C-S)
CLAY PRO-TECTED ORGANIC S (C-O-S) (C-S)
STABLE ORGANIC S (C-O-S) (C-S)

Figure 1. A conceptual flow diagram of the main forms and transformations of sulphur in the soil-plant system (Bettany and Stewart 1983 and Maynard 1983).

Carbon:sulphur and HI-S:total S ratios of the soil organic matter can vary widely. Excess solution sulphate, leading to increased uptake of sulphate by microorganisms, could narrow the C:S ratio and increase the HI-S:total S ratio in the organic matter. This means theoretically that a considerable quantity of the incoming sulphate could be immobilized in soil organic matter. The extent of immobilization is related to microbial activity and solution sulphate concentration.

Similarly, when harvesting and cultivation practices, such as clear-cutting and replanting, affect the carbon balance in the soil, there is a potential for increased mineralization of organic sulphate, as has been found with soil organic nitrogen. Preliminary data from watersheds on N and S leaving the hydrological basin after clear-cutting consistently show a N flux but do not show similar S fluxes (Swank, personal communication). Research that looks at C, N, and S dynamics simultaneously is needed to understand this fully.

In conclusion, the S dynamics and transformations in organic matter need to be understood in greater detail before the full impact of sulphate in acid deposition can be understood and future effects predicted. The type of research needed involves following C, N, and S dynamics simultaneously in organic matter *and* running concurrent measurements on inorganic processes. Measuring one facet of the S cycle without looking at other processes can lead to erroneous results.

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DISCUSSION

Question: How much sulphate is eventually released as H_2S or as mercaptans? Is this related to soil moisture content and what is the relationship?

Answer: The evidence that exists for the conversion of sulphate to sulphides and release of H_2S or mercaptans mainly comes from work in marshlands or in flooded paddy soils. As sulphides precipitate in flooded soils as copper sulphides and zinc sulphides, the rate of transfer is difficult to measure: the net release of the gases will depend on the physical and chemical properties of the soil. The release of sulphur to the atmosphere from soils usually occurs under anaerobic conditions.

There has not been much work on the loss of S as H_2S or as mercaptans from agriculture and forest soils under natural environmental conditions. However, in the laboratory, soils have been incubated aerobically and anaerobically with and without plant S amendments and estimates made of sulphur losses (cf. Banwart and Bremner, 1975, 1976a, 1976b). Of 25 soils in one study, 14 released some S compounds under anaerobic conditions and only four under aerobic conditions. Sulphur compounds released were identified mainly as dimethyl sulphide, with traces of carbonyl sulphide, carbon disulphide, methyl mercaptan and dimethyl disulphide, but no H_2S. Losses did not exceed 0.05% of the total S in soil which would be negligible in practical agriculture. Addition of amendments to the incubating soils increased losses as follows: sewage sludge increased losses to 0.2%, animal manures to 0.5%, several plant remains to 3.4%, and sulphur-rich cruciferous plants to 15.6%.

Swaby (1980) reports on Australian work involving 56 temperate and 30 tropical soils which were amended, moistened or waterlogged and incubated in the laboratory for 10 weeks when the evolution of H_2S was measured. H_2S was rarely detected from aerobic incubations, but H_2S could be detected in amended soils, generally under waterlogged conditions. However, although H_2S was generated more frequently under waterlogged conditions, its volatilization was often less than from open pores in aerobic soils. From this work, Swaby (1980) estimated that the greatest volatile loss of hydrogen sulphide from arable soils would not exceed 0.12% of the added S per annum, which is agriculturally insignificant compared with leaching losses as sulphate.

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TECHNICAL SESSION V
EFFECTS OF ACID RAIN ON SOIL PROCESSES

Acid Rain Effects on Nitrogen Availability from Litter and Organic Matter Decomposition

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ABSTRACT

The combined effects of various nitrogen transformation processes in soil in relation to the nature of the plants or trees have to be taken into consideration in evaluating the availability of nitrogen in any ecosystem. The same edaphic factors that affect plant growth also influence nitrogen transformation processes and ecological stability. Litter decomposition and organic matter turnover are also integral parts of the cycle that limits nitrogen availability to trees. Normal growth and development of forest stands, therefore, depend on the continuity of all the inter-related processes that influence nitrogen availability. Acidification of forest ecosystems from external sources can affect chemical and biological nitrogen transformation processes within trees, in the soil, and also in the atmosphere. Data on nitrogen availability in acidified forest ecosystems indicate both favorable and deleterious effects of acidification.

INTRODUCTION

Nitrogen is well established as the most important factor limiting the growth of trees in the forests of the northern temperate region and needs no substantiation with citations. Nitrogen has earned this reputation, not because of its scarcity in the nutrient pool under the temperate forest stands, but because of its limited availability to growing trees. In most podzolic soils, the nitrogen reserve in the organic horizons amounts to many times the quantities of nitrogen in the standing crops (Cole and Rapp 1981; Weetman 1961). Table 1 shows values for nitrogen reserves in the organic horizons under some temperate forest stands and the amount in the crops themselves. Nitrogen reserves in organic soil horizons are generally large enough to support tree growth through more than two rotations. Thus, the restricted availability potential of N under forest stands is the result of reduced rates of N transformation processes, which are responsible for the conversion of the organic forms of nitrogen compounds into mineral forms readily absorbable by the trees. In addition to large reserves in organic matter, nitrogen is added to the soil by precipitation, dry deposition, and fixation either by free-living microbes or by those associated with plants. Various environmental factors influence different N ecosystems. The ubiquitous nature of acid rain problems suggests an additional factor on the list of variables influencing N transformation process and input. Thus, the problems involved in evaluating nitrogen availability potential have been complicated by the effects of acid rain.

Table 1. Average values for nitrogen in trees, forest floor, and litterfall materials in the forest of different regions (after Cole and Rapp 1981)

Forest region	Tree		Forest floor		Litter N returned $kg\ ha^{-1}\ yr^{-1}$
	Biomass	Nitrogen	Biomass	Nitrogen	
	$kg\ ha^{-1}$				
Boreal coniferous	51 000	116	113 720	617	2.9
Boreal deciduous	97 000	221	68 772	548	20.2
Temperate coniferous	307 000	479	74 881	681	36.6
Temperate deciduous	152 000	442	21 625	377	61.4
Mediterranean	269 000	745	52 343	515	34.5

The ultimate consequences of continued acidification of our terrestrial ecosystems have been recognized throughout the world, as evidenced by numerous international conferences and meetings organized to evaluate the problem and to seek possible solutions. Efforts are also being made to sensitize the public to the grave nature of these problems. The effects of acid rain on N transformation processes is one of the topics addressed at most meetings. Alexander (1980 a,b), in his presentations at two recent meetings (one in Canada and the other in Sweden), pointed out the biological implications of acidification for the nitrogen cycle of our terrestrial ecosystems. International experts who gathered recently to discuss the fate of nitrogen and the roles of microorganisms in nitrogen cycling processes in terrestrial ecosystems (Clark 1981) again reiterated the need to understand N transformation processes. The resulting publications provide sound background information on what is already known about nitrogen cycling and how terrestrial productivity is dependent on N transformation processes.

Here, an attempt is made to review the existing literature on the effects of acid rain on nitrogen availability as represented by litter and organic matter decomposition. This presentation consists of a discussion of sequential processes of nitrogen transformations starting with nitrogen input to ecosystems via dry and wet deposition, continuing with fixation, leaching of litter materials, breakdown of litter and organic materials, and potential availability of nitrogen to forest trees during various phases of litter and organic matter decomposition. The role of microfauna and microflora on the decomposition processess as influenced by acidification of the ecosystem is also discussed. Finally, some data are presented concerning acid rain effects on N transformation processes and the role of other factors on these processes.

NITROGEN AVAILABILITY AND INPUT

Nitrogen Availability

The term "available nitrogen" has been used to represent the quantity of mineral nitrogen (NH_4 + NO_3) in the soil organic horizons. The quantity of mineral nitrogen in soil is a dynamic entity depending upon several variables (Mahendrappa 1980). Yet in numerous publications on the modeling of nitrogen cycles in ecosystems, the quantity of mineral N extracted from samples collected at a particular time has been used to represent available nitrogen. Availability of mineral N to trees depends on the proximity of the roots to the pool of mineral N, on competition, and on other agents, such as microbes. Thus the quantity of mineral N determined using a standard method can be considered to represent potentially available N (as an index only). The concept of "available nutrient" has been used to determine the quantity of fertilizer to be applied. The quantity of nutrient available from the soil is subtracted from the nutrient requirements of the crop to calculate the quantity of fertilizer required. Using this concept, Fried and Dean (1952) developed a term called an "A-value" to represent the quantity of phosphorus available in the soil. A similar formula was adopted by Broadbent (1970) to characterize variables affecting soil nitrogen availability. New approaches to determine nitrogen availability index were tested by Stanford and his numerous colleagues (Stanford et al. 1975; Stanford 1981). All these tests are applicable to agricultural crops; the results do not necessarily apply to forest ecosystems. A recent review by Keeney (1980) on the subject of prediction of soil nitrogen availability in forest ecosystems clearly points out the need to consider factors in addition to those used in agriculture. A need for considerable research effort into characterizing the nitrogen cycle in forest ecosystems is stressed in his review. Combinations of chemical and microbiological assays to determine potentially available nitrogen in forest soils have been investigated by several workers, and some results are quite promising (Wollum and Davey 1975; Verstraeten et al. 1970; Nommik 1976; Mahendrappa 1980). More research should be carried out to estimate more reliably the quantities of potentially available nitrogen in the forest ecosystems, which would have to be established before evaluating the effects of acid rain on potentially available nitrogen. In recognition of this fact, a discussion paper was presented at the Sixth North American Forest Soils Conference held in Tennessee, June 1983.

Nitrogen Input

Nitrogen is added to ecosystems in a number of processes. Nitrogen may be input directly from the atmosphere in the form of wet or dry deposition. Under unpolluted conditions elemental nitrogen is converted to ammoniacal nitrogen (NH_3) or oxides of nitrogen (NO_x) through photochemical reaction or lightning (Dawson 1980). The quantity of nitrogen added in this form appears to vary from 2.6 kg N yr^{-1} to 10 kg N yr^{-1} (Mahendrappa and Ogden 1973; Carlisle et al. 1966; Nihlgard 1970; McColl et al. 1982). Part of the ammonium N in precipitation may be derived from natural volatilization of ammonia from the Earth's surface (Dawson 1977; Environment Canada 1981). Following the increased use of fossil fuel for the production of energy, nitrogen (and sulfur) loading of the atmosphere has increased substantially. The quantity of nitrogen ($NH_4 + NO_3$) in the air or reaching the ground or plant surface in the form of wet or dry deposition can vary considerably depending on the quantity of fossil fuel consumed, its nitrogen content, and the directional distance from the point where the fuel is burned. Increases of 100 to 1000% in nitrogen concentration in precipitation have been documented (Canada-U.S. Coordinating Committee 1983). In heavily impacted areas nitrogen inputs as high as over 20 kg N ha^{-1} yr^{-1} have been reported (Heinricks and Mayer 1977; Likens et al. 1978). Such additions have resulted in an increase in the quantity of available (mineral) nitrogen to forest ecosystems. Experimental work carried out to study the effects of simulated acid rain on plant growth with NH_4 and NO_3 levels similar to those in polluted areas have resulted, in many cases, in stimulation of growth. Such a stimulus is attributed to high nitrogen content of simulated rain water.

Under natural conditions varying amounts of nitrogen are added to forest soils by different nitrogen-fixing agents. These include symbiotic nitrogen fixers such as alders (Akermans 1979) free, living bacteria (Knowles 1974), and lichens (Denison 1979; Denison et al. 1976). All these N fixers are sensitive to pH changes in the soil. Thus, the quantity of nitrogen added in this form to the forest ecosystem is dependent on tree species and location.

NITROGEN TRANSFORMATION PROCESSES

Forest trees absorb most of their mineral nitrogen from the soil in the form of ammonium ions, as compared with agricultural crops that absorb mostly nitrate N (McFee and Stone 1968). Thus in forest ecosystems, the slow rate of nitrogen transformation processes leading to the formation of ammoniacal (mineral) N limits its availability to trees. There is evidence to indicate that forest trees do absorb some organic nitrogen compounds directly before mineralization (Miller 1968).

Microbiological N Transformations

Most of the nitrogen transformation processes are mediated by various microbes. The most important N transformation process that affects nitrogen availability in forest soils is the continuous and dynamic mineralization-immobilization actions. Microbial agents directly responsible for these processes include bacteria, fungi, and actinomycetes (Alexander 1980a; Berg and Staaf 1981; Abrahamsen 1980a,b). Work carried out to determine the effect of increasing acidity on microbial agents responsible for N transformation (Berg and Staaf 1981) indicates that no significant changes occur in fungal biomass due to high acidity. Manometric oxygen consumption studies show decreasing microbial activity due to lower pH created by the addition of S and pre-incubation for 6 months (Salonius and Mahendrappa 1979). Net mineralization (the difference between mineralization and immobilization), as measured by alkaline distillable N in autoclaved samples (Mahendrappa 1980) or KCl-extractable ammoniacal N, shows decreased values for potentially available N in the raw humus materials acidified *in situ* due to SO_2 emission.

Although forest trees preferentially absorb ammoniacal nitrogen, nitrate N is absorbed and used as a source of N. Also, nitrification of ammoniacal N in forest soils may result in decreased availability of nitrogen because of its easy leachability beyond the root zone. Therefore it is necessary to consider nitrification as one of the processes affecting nitrogen availability in forest soils. Factors affecting nitrification in acid forest soil organic horizons are not well understood. The highly acidic conditions that exist in most conifer forests of the temperate region are generally considered unsuitable for conventional nitrifying bacteria. Nitrate formation, however, has been recorded in highly acidic black spruce raw humus (organic horizons) both under field conditions (Mahendrappa and Salonius 1982) and in samples incubated under laboratory conditions (Roberge and Knowles 1966). High nitrate levels in streams in forested and clear-cut areas have been recorded by various workers (Bormann and Likens 1967; Krause 1982; Galloway and Dillon 1983). High nitrate levels during early spring thaws have also been documented by several workers. Nitrate accumulation in snow as a result of dry and wet deposition of NO_x is generally considered the probable cause of this upsurge of nitrate levels in streams during spring thaws (Galloway and Dillon 1983; Scheider and Dillon 1983). The occurrence of nitrification in the organic horizons under the snow has also been recognized as a source of high nitrate N in streams during the spring thaw (McBrayer and Cromack 1980). Under such situations, the limited root uptake and increased leachability of nitrate may cause a higher proportion of nitrogen to be lost from forest ecosystems.

Under field conditions, nitrification occurs when ammonium ions are present in high concentrations and when root and microbial competition for mineral N is absent (Mahendrappa and Salonius 1982). Such a situation can arise during extremely dry conditions or following the application of high doses of fertilizers. Both extremely dry conditions of organic horizons under forest stands and the application of fertilizers may raise the pH of acid organic horizons to levels more suitable for nitrifiers to operate. Also, under these conditions toxic or inhibitory organic compounds may be removed through increased solubilization and leaching from organic horizons. A combination of the above conditions may be necessary to promote nitrification in highly acidic organic forest soils. With continuous addition of hydrogen ions by wet and dry deposition, the chances of nitrification taking place in the organic horizons of the forest soils seem remote. Thus, the loss of NO_3-N through leaching will be negligible under normal forest conditions.

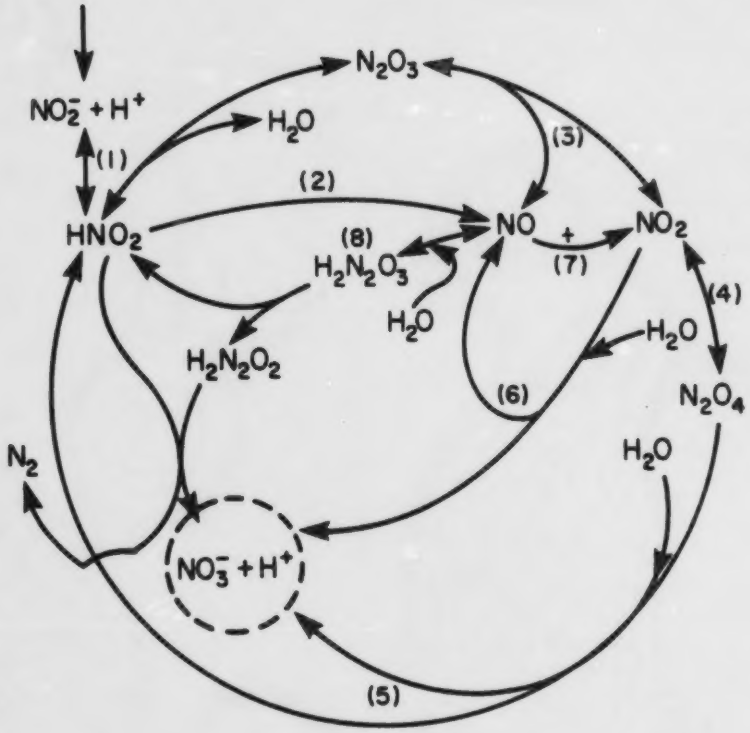
Denitrification, which is the reduction of nitrate and nitrite to reduced forms of nitrogen, such as N_2O, N_2, and ammonium, is chiefly a biological process. Conversion of readily absorbable nitrate and nitrite to gaseous (N_2O, N_2) products leads to decreased N availability. The significance, proportion, or the environmental conditions favoring the reduction of nitrate and nitrite to ammoniacal N are not well understood (Tiedje et al. 1981). Higher pH favors microbial denitrification in which the end product is N_2O or N_2 (Knowles 1981). According to Focht's (1974) conclusions based on the data of Nommik (1957) and Wijler and Delwiche (1954), the rate of microbial denitrification (K) varies linearly with the pH of the medium and is inversely related to the percent pore space in the soil filled with oxygen. In the present author's studies, no denitrification products were found when organic horizons from a black spruce stand were incubated for up to 6 months under anaerobic conditions and moisture saturation. Neither pH nor redox potential measured during the 6 months of incubation were low enough for denitrification to occur. From this, it is reasonable to assume that dissimilatory denitrification in acid soils may not severely influence the availability of nitrogen. At the same time the data (Focht 1974) show that, at very low pH, the proportion of N_2O produced is very high.

Chemical N Transformations

Parallel to the microbial actions are chemical and physical processes that can also lead to various nitrogen transformation reactions. These result in the formation of gaseous N compounds. These may also have the ability to decrease N availability while increasing the danger of polluting air and water. Physical processes such as wetting and drying, freezing and thawing, and radiation have been shown to affect the level of mineral N in the soil (Birch 1960; Salonius et al. 1967, 1970; Salonius 1972). No information is available on the influence of acidity on these processes.

Fixation of ammonium ions by the colloidal fractions of soils renders this form of nitrogen unavailable for plants or microbes (Nommik 1981). In his review paper, Nommik (1965) pointed out that the data on N fixation in 200 surface soils from Sweden showed a tendency for chemical NH_4 fixation to increase with increasing pH. Apparently at pH below 5.7, chemical ammonium fixation becomes negligible. Roberge (1972) found higher proportions of ammoniacal N in solution and less in the exchangeable form in black spruce organic horizons adjusted to low pH. The amount of ammoniacal N in solution was inversely related to pH of the medium. Thus, at low pH, more ammonium N may be potentially available for plant growth. This mechanism may have been involved in stimulating tree growth and high N uptake in a field experiment in Sweden where Nommik (1981) applied 96 kg ha^{-1} of sulfuric acid (Tamm and Wiklander 1980).

Under strongly acidic conditions both nitrification and denitrification reactions take place (Mahendrappa 1966, 1972, 1974; Knowles 1979). When either nitrate or nitrite decomposes under acidic conditions, an array of oxides of nitrogen are formed (Yost and Russell 1944). Most of the oxides of nitrogen, being thermodynamically unstable, are further converted to a few stable compounds. In fact, a large proportion of nitrite can be converted to nitrate (Fig. 1; Mahendrappa 1966), thus causing chemical nitrification. In such a sequence of reactions, a portion of the nitrite can also become either elemental nitrogen or oxides of nitrogen. In one study, the proportion of nitrite or nitrate lost to the atmosphere from the organic horizons under a black spruce stand was shown to be less than 0.1% of the nitrate added (Mahendrappa 1974). Thus, in summary, the chemical reactions of nitrification and denitrification processes are found to be more active at low pH values. Because of these reactions more N can be lost or its availability reduced. Most of the thermodynamically feasible reactions between the oxides of nitrogen that occur in the above-ground atmosphere are also active in the below-ground atmosphere of the acidic forest soil organic horizons.



$NO_2^- + H^+$
(1)
H_2O
N_2O_3
(3)
(2)
HNO_2
(8)
$H_2N_2O_3$
NO
+
(7)
NO_2
(4)
H_2O
H_2O
$H_2N_2O_2$
(6)
N_2O_4
N_2
H_2O
$NO_3^- + H^+$
(5)

1. pH sensitive
2. Hastened by both organic and inorganic soil components
3. Equimoles of NO and NO_2 produced
4. Instantaneous process
5. Equimoles of products formed
6. Temperature, sensitive gas phase reaction
7. Instantaneous aerobic reaction
8. Extremely unstable in acid media

Figure 1. Possible pathways for the transformation of oxides of nitrogen in acid media (from Mahendrappa 1966).

LITTER DECOMPOSITION

Changes occur in litterfall materials from the initiation of senescence. Nutrients in the foliage are retranslocated to other parts of the trees to be stored until the next growing season. Larger amounts of N than any other nutrient are retranslocated before leaf fall. Ostman and Weaver (1982) found that 77% of the nitrogen present in the leaves of an oak (*Quercus* sp.) stand were retranslocated before leaf fall. The efficiency of retranslocation appears to be species dependent (Cole and Rapp 1981). Conifers of the boreal and temperate regions retranslocate a higher proportion of N than deciduous trees in these regions. There are no data on the effects of acid rain on the proportion of N in retranslocated foliage. However, with reduced availability under acidic conditions (coniferous forest), the retranslocation of N may be in relatively greater proportion than under less acidifying conditions (deciduous forest).

Leaching of nutrients from the foliage by rain takes place throughout the growing season. The quantity of N leached from foliage is mainly a function of foliar N concentration. The greater the foliar N content, the greater is the quantity of N leached for both hardwoods and softwoods. Hydrogen ions in rain water enter into exchange reactions with other cations in needles, and the displaced cations are easily washed off (Mahendrappa 1983). The quantity of cations displaced from the needle litter depends on the hydrogen ion concentration of the rain. Thus, as rain acidity increases, larger quantities of cations can be leached from the foliage (Yawney et al. 1978). The ammonium ion, being a positively charged ion (cation), can be leached in increasing quantities as rain acidity increases. These reactions occur when the needles are either on the tree or on the ground as litter.

Litterfall materials reaching the ground undergo further leaching before they are significantly acted upon by microfauna, fungi, or bacteria. According to Bäath and Söderström (1980) it took a year before the fungal population in Scots pine needles reached a maximum. Thus a considerable proportion of N can be leached during that period. Nykvist (1963) found that 15% of the nitrogen in a *Fraxinus* sp. foliage could be leached with water. Mahendrappa and Ogden (1973) found that 5% of the total N in fresh black spruce (*Picea mariana* ([Mill.]) B.S.P.) litter materials could be leached with distilled water. Combined effects of nutrient retranslocation and leaching from foliage and freshly fallen litter materials have been shown to reduce the total N content of litter to about 60% of the level in the current year's foliage of several species (Mahendrappa and Kingston 1980, Fig. 2). This value could increase as rain acidity increases.

There is no doubt that retranslocated nutrients, including nitrogen, are directly used by the trees. Nutrients leached from foliage and fresh litter can also be readily available to the trees. This depends, however, on the activity of the roots in the organic horizons and the moisture status of the organic horizons. The roots should be able to compete with microbes for the nutrients leached from litter during the growing season. The moisture status of the organic horizons affects both the root and microbial activities and the flow rate and residence time of the nutrients. The significance of the effects of rain acidity on the loss or recirculation of nutrients in fresh litter materials is not known.

Litterfall materials, after reaching the ground, are comminuted by the soil microfauna during their feeding process. The materials ingested by insects and other microfauna are enriched with N. With higher N concentrations the fecal materials have a greater potential to release mineral nitrogen than do litter materials not acted upon by microfauna. The acid rain effects on the microfaunal population are not favorable (Abrahamsen et al. 1980; Bath et al. 1980; Lohm 1980; Francis et al. 1980). However, the populations of some microfauna, such as mites, are apparently unaffected by acid treatments for short periods (Hagvar 1980). The long-term effects of chronic acid rain on the microfauna that break down litter materials are not known.

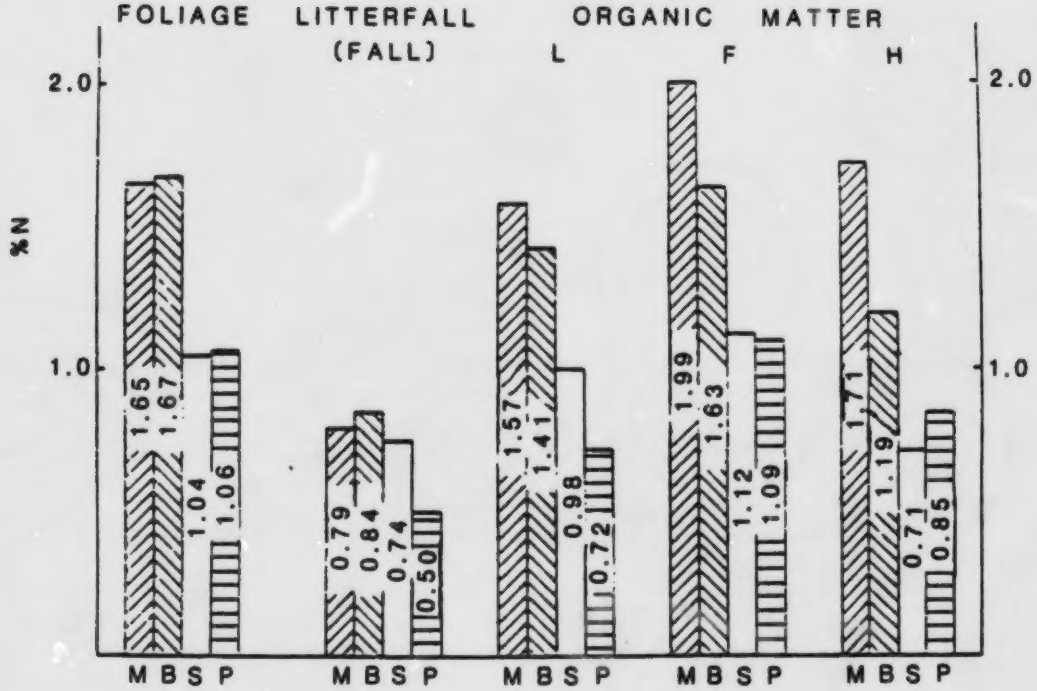


Figure 2. Concentrations of nitrogen in the foliage, litterfall materials, and the organic (L, F, and H) horizons under two hardwood (M = Maple, B = Birch) and two softwood (S = Red Spruce and P = Red Pine) stands (from Mahendrappa and Kingston 1980).

Several workers have investigated the decomposition of litterfall materials by measuring their weight loss during field or laboratory incubation. Exposing litter materials to low levels of SO_2 before incubation has led to increased acidity and a slower rate of decomposition than in unexposed materials (Killham and Wainwright 1980; Dodd and Lauenroth 1981; Leetham et al. 1983). According to these workers, the reduced decomposition was probably caused by reduced pH or accumulation of toxic derivatives of SO_2 in the microenvironment of organisms on the decaying leaf surfaces. Nitrogen levels in litter materials may also influence the rate of litter decomposition (Salonius and Mahendrappa 1975). These data, however, do not help determine the quantities of nitrogen released in available form during litter decomposition.

ORGANIC MATTER DECOMPOSITION

In forest ecosystems, it is difficult to make a clear distinction between partly decomposed litterfall materials and extensively transformed organic matter in the organic horizons. Under both hardwood and softwood stands, recognizable leaf materials can be found in the L and F horizons. Here, for the ease of discussion, the recognizable leaf materials are not distinguished from other organic horizons with respect to their N-supplying potential.

The decomposition of organic matter is predominantly a microbiological process, especially when dealing with potentially available nitrogen. Some of the biochemical reactions that occur during the formation of humic and fulvic compounds generally lead to the formation of more complex compounds in which nitrogenous compounds are bound in forms unavailable to plants. Thus the process of organic matter breakdown comprises two phases: 1) the microbial breakdown of organic residues of plant and animal origin, and 2) the breakdown of complex organic compounds by way of either microbial or physico-chemical processes. Since the physico-chemical process of organic matter decomposition has been dealt with earlier, only the microbial process is discussed in this section.

The decomposition curves for individual constituents of forest litter materials have been established by Minderman (1968) (Fig. 3). These hold true for the decomposition of complex organic compounds also (Stevenson 1982), as long as some energy source is available for the microbes to initiate decomposition (Mahendrappa 1978; Salonius 1972). There are two points to be recognized in this graph (Fig. 3): 1) the easily decomposable compounds do not contain nitrogen, and 2) phenols are the most resistant compounds. Thus, during the initial stages of decomposition (or weight loss in the case of partly decomposed litter materials), nitrogen enrichment of the organic matter takes place (Staaf and Berg 1977, 1981; Mahendrappa and Kingston 1980). Our data presented in Figure 2 show that nitrogen levels in the L, F, and H horizons under both hardwoods and softwoods have increased to the levels found in live foliage. Thus the litterfall materials, apparently, have undergone considerable N enrichment during decomposition. Gosz (1981) stated that soil organic matter rich in phenols and their derivatives decomposes more slowly. Some evidence suggests that under acidic soil conditions and low nitrogen availability, the foliage produced is rich in phenolic compounds. The polyphenolic compounds, being water soluble and antiseptic to microbes (Morita 1975), tend to slow down organic matter breakdown. Data from organic horizons acidified *in situ* to different degrees by SO_2 pollution support this hypothesis (Fig. 4). Samples from areas severely affected by SO_2 generally contain larger concentrations of polyphenols than the organic horizons in the unaffected areas. In samples from the severely affected areas, microbial activities were also severely reduced. In the L horizon of the severely affected areas, the pH had dropped below 2. When urea was added and the samples incubated under laboratory conditions, little ammonia was volatilized compared with in samples from the moderately affected area where pH remained above 3. These results agree with those of Killham et al. (1983).

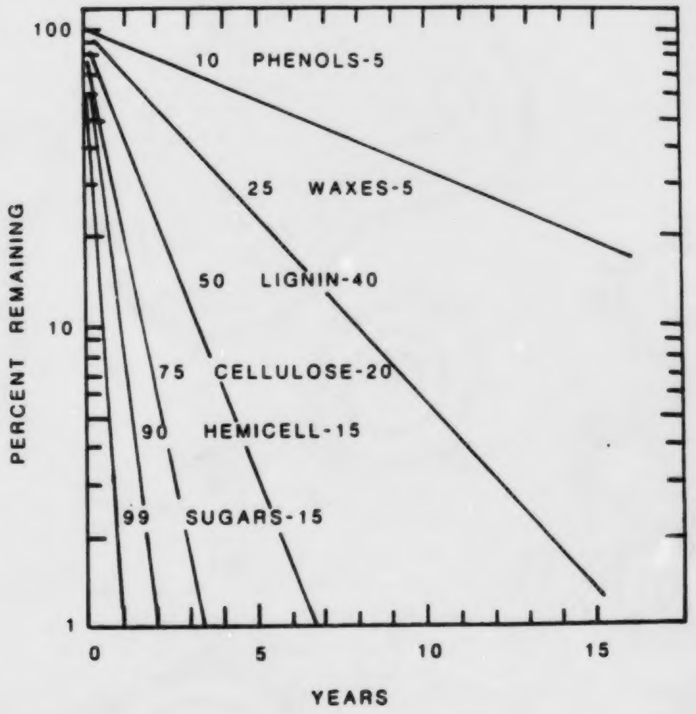


Figure 3. Decomposition curves of various organic compounds in the soil. The numbers before and after the names of compounds represent, respectively, the proportion lost in a year and its weight as a percentage of the original litter material (from Minderman 1968).

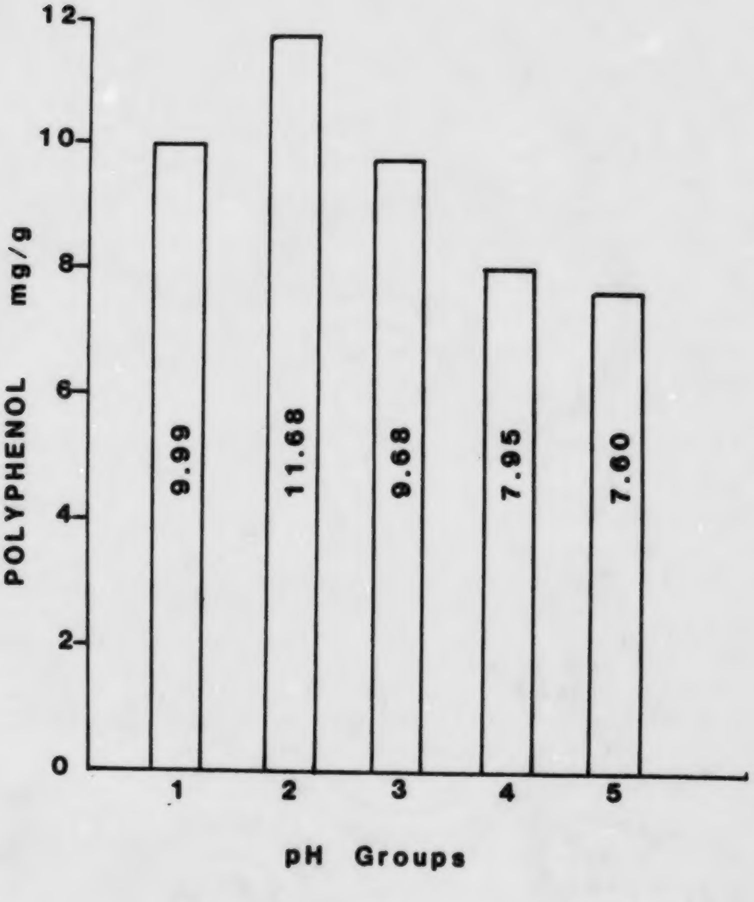


Figure 4. Measured quantities (mg g^{-1}) of polyphenols extracted with pyrophosphate from organic horizons variously affected by SO_2 pollution (1 = pH <2.5, 2 = pH 2.5-3.0, 3 = pH 3.0-3.5, 4 = pH 3.5-4.0, and 5 = pH >4.0).

Organic materials rich in polyphenols decompose at a slower rate than those low in polyphenols. Stark (1971) found accumulations of organic matter up to 2 m deep in tropical podzols having good drainage and excellent conditions favoring fast decomposition of organic material. The polyphenol content of organic material on such sites was higher than that in an adjacent latosol that had a thin (a few centimetres) organic horizon. Williams and Gray (1974) suggested that the polyphenol content determines differential rates of litter decomposition, and the effect is influenced by pH of the litter and soil nutrient status. Gosz (1981), in his review, has summarized the interdependence of soil and foliar N status, polyphenol content, and the buildup of organic matter. His results agree with our data on the organic horizons differently affected by SO_2 pollution.

A few words of caution are warranted here to avoid misinterpretation of the data on, and the role of, polyphenols in organic matter decomposition. The methods employed for the determination of polyphenols do not distinguish between different phenolic compounds. Not all the phenolic compounds at a given concentration are inhibitory to microbes to the same degree. The concentrations of water-soluble phenolic compounds in the foliage or in litterfall materials do not necessarily represent the level of phenolic compounds in the organic horizons. Polyphenols resulting from the degradation of lignins in plant residues undergo various chemical changes, such as polymerization or condensation, that result in the formation of compounds more resistant to decomposition (Stevenson 1982). The effects of acid rain on the formation or breakdown of phenolic compounds in the foliage or in the organic horizons have not been ascertained.

Trees grow even when thick organic horizons have accumulated under the stands, which indicates that some mechanisms have evolved to permit nutrient absorption under these conditions. The increased acidification of our forest ecosystems may be hastening the buildup of thick organic horizons with high polyphenol content. The means of increasing nutrient uptake and reducing organic matter buildup should be understood. In forests with slow decomposing polyphenol-rich organic matter, the process of mineralization of organic N compounds may be circumvented, and the soluble organic N compounds directly absorbed by the tree roots. Such absorption of soluble organic N compounds is facilitated by mycorrhizal fungi (Heal et al. 1982). Thus, it may not be necessary for the mineralization process to occur before nitrogen and other nutrients in the organic horizons become available to trees in forest ecosystems.

Plant and animal residues in the soil undergo decomposition, liberating CO_2 during the process. This process enriches the remaining material with nitrogen (Fig. 2). The F and H horizons are rich in humic and fulvic compounds that contain varying proportions (0.5-3%) of nitrogen (Stevenson 1982). Fulvic compounds, which are soluble at pH levels normally found under forest stands, can form a source of soluble organic N compounds that may be absorbed directly either by the roots or through the mycorrhizal fungi. Extensive proliferation of fine roots and mycorrhiza makes up for small proportions of fulvic compounds that become soluble at any time. Mahendrappa and Salonius (1982) found that organic nitrogen in the soil solution did not show variations between sampling periods or between plots treated with different fertilizers. Thus, the size of the soluble organic N pool may be maintained despite constant absorption by fine roots and mycorrhizal systems associated with roots (Bowen and Smith 1981). A considerable amount of nitrogen in the humic and fulvic acid components of the organic matter can constitute a ready source of available N for tree growth.

DISCUSSION AND SUMMARY

It is an indisputable fact that nitrogen availability limits tree growth in the forests of northern temperate and boreal regions. We do not completely understand all the factors and interactions responsible for reduced availability of nitrogen in these forests. Anthropogenic sources of acid rain falling on the forests of temperate and boreal regions have increased the complexity of the problem.

In forest ecosystems, unlike agricultural systems, the term nutrient availability has not been well defined. Organic horizons built up on the mineral horizons under forest stands tie up a large quantity of nitrogen in organic form generally unavailable to trees. Most of the actively feeding roots of conifers are located in the organic horizons, suggesting that a major portion of the nitrogen taken up by the trees is derived from these organic horizons. The method used in agricultural systems to measure potentially available N in the mineral horizons is not applicable in forestry. The populations of microflora and microfauna in the forest organic horizons are, in most respects, different from those in agricultural soils. The organic horizons under forest stands rarely reach the air-dry state as compared with agricultural soils that often become air-dry. In spite of these and other differences between forest organic horizons and agricultural soils, the methods developed for agricultural systems are used in forest ecosystems. This situation has to be remedied.

Numerous stations established to monitor wet and dry deposition in Canada and the United States are not intended to provide information on the quantities of various chemicals, including nitrogen, deposited in individual forest ecosystems. Even if precise data are available on the quantities of hydrogen ions and nitrate and ammonium N deposited per unit area, we are not able to predict the fate of these chemicals. Documentation of the partitioning of these chemicals, as the rain penetrates through the forest canopy, has not been accomplished. Furthermore, the possible reactions of nitrate N with the organic matter are not understood. Galloway and Dillon (1983) suggest that the proportion of nitrate N retained in the organic horizons and taken up by the roots is dependent upon the hydrological residence time. If short, a higher proportion of nitrate N is assumed to be transported to lakes and streams. Our data, on the other hand, show that nitrate N is retained by the organic horizon, probably on the anionic exchange sites of the complex organic molecules (Schnitzer 1980), and the proportion of it leached is a function of the volume of water flow and its chemical characteristics. The proportion of nitrate N leached with HCl from the incubated organic horizons was less than that leached with calcium hydroxide solution (Fig. 5).

Chemical reactions of nitrate and nitrite ions in acid media can result in the production of various other oxides of nitrogen and elemental nitrogen. These reactions are catalyzed by transition metals whose solubility increases with increasing acidity. The significance of these reactions in forest ecosystems is not well understood.

Nitrate N is formed within the forest organic horizons via microbial and chemical processes. Apparently these processes occur in microsites with environments conducive to nitrification. Nitrification is reported to take place under snow cover. The fate of nitrate N formed under various conditions is different, as is the relative availability of nitrate N to forest trees.

Nitrogen transformation in decomposing litter occurs in three phases: leaching, enrichment, and release due to breakdown of organic compounds. Prior to leaching, extensive retranslocation of nitrogen from foliage to other tree components occurs. The significance of both retranslocation and leaching of nitrogen from foliage is not clear. Acid precipitation is known to increase the leaching of nutrients including nitrogen from foliage and litter. However, there is no information on the fate of nitrogen leached in this manner. It seems reasonable to assume that the nutrients, nitrogen in particular, would be more available under acidic conditions (Roberge 1972; Tamm and Wiklander 1980).

Enrichment of litter materials with respect to nitrogen is the result of consumption of carbon compounds by soil invertebrates and populations of bacteria, fungi, and actinomycetes. Acidification of the medium (organic horizons or litter materials) has been studied by several workers. Acidification is reported to decrease the rate of weight loss of litter materials by decreasing both the microbial and microfaunal activities. Conflicting results have been obtained on the effects of acidity on the populations and biomass of fungi and microfauna such as collembola, mites, etc. The mechanism involved in reducing the activity of either microflora or microfauna in the soil has not been elucidated.

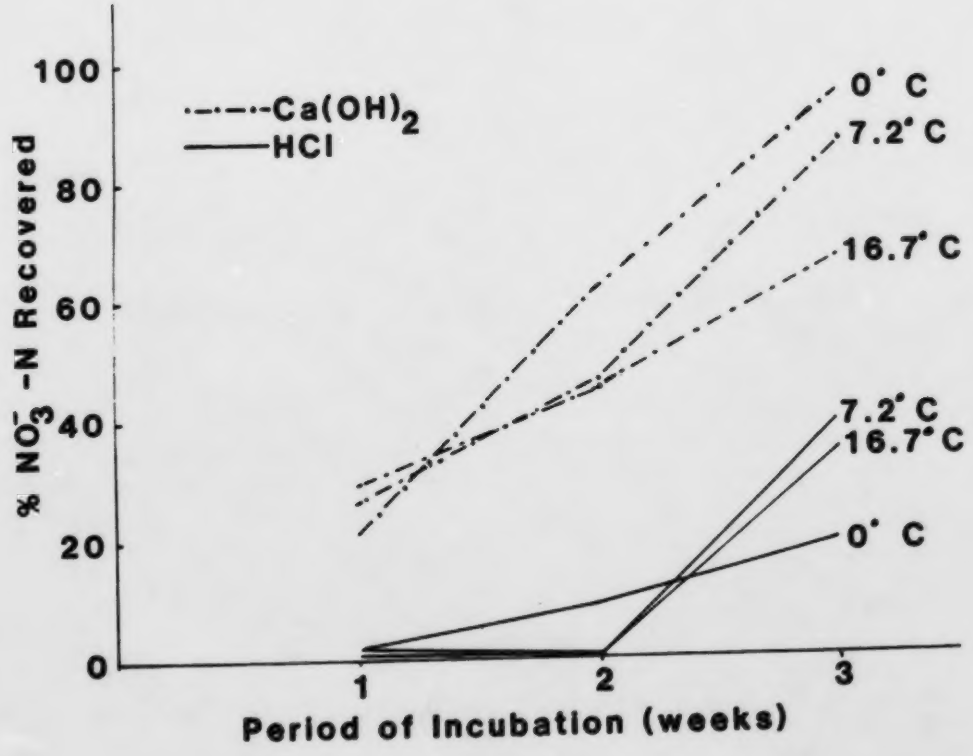


Figure 5. Recovery of nitrate N from black spruce raw humus materials when extracted with 1 N HCl and saturated Ca $(OH)_2$ solution.

Organic matter decomposition represents the third phase of litter decomposition. The process of organic matter decomposition under forest stands is different from that in agricultural soils. The mechanism of nutrient uptake by forest trees also appears to be slightly different from that of agricultural crops. The trees are probably capable of absorbing organic nitrogenous compounds directly, thus partly circumventing the need for the mineralization process. These observations suggest that the information available on the effects of acid rain on the potential availability of N to trees from the decomposing litter and organic materials has to be interpreted with caution. There is limited information on the behavior or fate of nitrogen and its organic and inorganic compounds in organic horizons under forest stands.

At present, various researchers have shown a positive effect of acid precipitation on tree growth (Tamm and Wiklander 1980; Abrahamsen 1980a). This may be due to increased levels of mineral N in solution (Roberge 1972) or increased N mobilization (Tamm 1982). Such an effect may be more evident and less serious in the northern boreal and temperate region than in the south. However, Abrahamsen (1980b) concludes that the long-term effects of continued acidification of our ecosystem may be deleterious to both forest and soil systems. Tree growth may be severely reduced, and forest soils may be extensively degraded partly because of decreased nitrogen transformation processes and decreased availability of N to trees. There may also be a general decrease in the availability of other nutrients and increased acidification of streams and lakes.

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DISCUSSION

Question: Do you have quantitative data on the extent of nitrification in typical forest soils of eastern Canada — that is, nitrate production in kg N ha^{-1} yr^{-1}?

Answer: I do not know of any such data for typical forest soils of eastern Canada. As I pointed out, we have found nitrate N under both field and laboratory conditions. I do not think it is safe to convert such values, measured in the soil solution for which we do not have quantitative data on the volume, into kilogram quantities. Incubated soil samples produce up to 100 kg NO_3-N ha^{-1} yr^{-1} on an oven-dry-weight basis. But the quantities of nitrate-nitrogen produced were different among L, F, and H horizons. This morning Dr. Ulrich pointed out that nitrate formation in the field was found after dry conditions. We had to have a dry period before we could detect nitrate-nitrogen in the soil under field conditions.

Effects of Acidic Precipitation on Foliar and Root Diseases, Soil-borne Pathogens, and Ectomycorrhizae of Forest Trees

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ABSTRACT

The chemistry of rain in much of the eastern United States has been modified to such an extent that levels of acidity considered insufficient for the inducement of acute botanical effects may significantly influence the epidemiology of numerous plant pathosystems.

Acidic precipitation may affect subtle host-pathogen interactions, hence modify otherwise predictable responses. Decreases in viability of pathogen propagules, alterations of their parasitic fitness, or direct injury to host plants may occur during or after episodes of acidic rain. Evidence suggests that acid rain renders fungal spores non-viable or destroys them during overwintering, dissemination, deposition, penetration, or colonization phases of their life cycles.

Effects of Simulated Acidic Rain on Fusiform Rust

Effects of simulated acid rain on the development of *Cronartium quercuum* f.sp. *fusiforme* were investigated. Two half-sib families of *Pinus taeda* were exposed to two episodes of simulated acid rain, both before and after inoculation with basidiospores of the rust fungus. Injury to needles (necrosis) was 0, 5, 27, and 60% in association with pH levels of 5.6, 4.0, 3.2, and 2.4, respectively. Six months after inoculation, means of 2.6, 1.6, 1.2, and 0.8 galls per 20 trees were observed at the same respective pH levels. A significantly greater number of trees exposed to the most acidic pH treatments exhibited "resistance traits". The number of trees expressing small "short" galls, reaction zones, rough galls, and infections with no galls was proportionately lower as pH treatments increased in acidity. These data suggest a radical alteration in pine-rust physiology as affected by acidic deposition.

Effects of Simulated Acidic Rain on Root Diseases and Soil-borne Pathogens of Forest Tree Species

Inhibitory Effect of Simulated Acidic Rain on Root Infection by Zoospores of *Phytophthora cinnamomi*

Rates of infection of lupine (*Lupinus angustifolius*) roots by *Phytophthora cinnamomi* (Pc) zoospores after single one-hour rain exposures decreased linearly with increasing rain acidity. Treatment means calculated for combined data from all three experiments were 56, 85, and 86% (for pH 2.4, 3.2, and 4.0, respectively) of the infection rate for pH 5.6 treatments.

Final pH values of water layers above naturally infected soil in beakers with solutions characterized by pH 4.0, 5.0, or 5.6 were all within the range of pH 5.07 to 5.62. However, water layers developed from pH 3.0 solutions had final acidity levels ranging from pH 3.85 to 4.11. With soil containing a high initial population density (high P_i) of Pc propagules, mean percentages of leaf disks floated on the water layers infected by Pc were 98, 99, 97, and 56% for pH 5.6, 5.0, 4.0, and 3.0 treatments, respectively. Roots of *Abies fraseri* seedlings were placed into the water layers above infected soil in each beaker. All seedlings expose to high P_i soil and the three highest pH treatments exhibited foliar symptoms typical of *Phytophthora* root rot six days after planting. Symptoms on seedlings exposed to pH 3.0 treatments in this test became apparent over a six- to 17-day period after planting, but one of the eight trees in this group never developed symptoms. In a low P_i test, mean percentages of leaf disks infected by Pc were 20, 21, 37, and 8% for pH 5.6, 5.0, 4.0, and 3.0 treatments, respectively. No seedlings developed disease symptoms during a 60-day period.

Inhibitory Effect of Simulated Acidic Rain on Asexual Reproduction by *Phytophthora cinnamomi*

Although absolute quantities of sporangia formed on lupine radicles were higher in the second of two identical experiments, the magnitude of the effect of rain solution pH on sporangium development was quite consistent. Equations of lines for normalized counts regressed on treatment pH were nearly identical. Compared to pH 5.6 treatments, sporangium production associated with pH 2.4 treatments was reduced by nearly half.

Populations of *Phytophthora cinnamomi* in Soil Columns Exposed to Simulated Acidic Rain

In columns exposed to pH 5.6 treatments, soil depth had no effect on mean Pc populations. However, mean populations varied directly with depth in columns exposed to pH 4.0, 3.2, and 2.4 treatments. Slopes of regression lines were greatest for the intermediate-pH treatments, suggesting that pH 2.4 treatments were affecting propagules even in the 4- to 8-cm deep layer. Similar trends were evident for measurements of effluent water pH collected from beneath columns at the end of the last exposure. Results suggest that, even though little effect of acidic rain was observed in 8-cm columns, Pc propagules in the upper 4 cm were subjected to changes by water that was only slightly buffered by shallower soil layers. Such changes are obscured when soil from this layer is mixed with deeper soil with unaffected populations.

Acid Rain Effects on Ectomycorrhizae of Forest Trees

Work is currently in progress for the purpose of quantifying these effects, and will be discussed in the context of forest productivity and pathogen interactions.

Evolution of Forest Soils of Quebec Under Acid pH Conditions*

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ABSTRACT

The large variety of Podzolic soils in Quebec, as illustrated by some typical profiles, depends on the nature of the parent material. The principal mechanisms responsible for the translocation of Al^{3+} cations released from primary minerals by protons are reviewed. The first mechanism involves the formation of organometallic complexes, but it cannot explain satisfactorily the formation of all types of Podzolic soils. The second mechanism considers that mineral aluminosilicate complexes, such as protoimogolite, are the main factors able to transport Al^{3+} down the profile.

Dissolution of primary minerals and their transformation into secondary minerals, as well as the further evolution of secondary minerals, are largely dependent on the leaching of M^+ and M^{2+} cations and on the final Al_2O_3/SiO_2 molar ratio. Podzolic soils in Quebec still contain a large supply of cations. Yet their ability to neutralize H^+ ions is determined by the availability of these cations and by the residence time of the percolating water. In the soils developed on till, saturated hydraulic conductivity is higher in the solum than in the parent material, and the solum is more depleted of cations.

Some relationships between soil properties and H^+ neutralization are discussed.

INTRODUCTION

In the province of Quebec, forest soils are located mainly in two physiographic areas, in the Appalachian Highlands to the south, and in the Laurentian Highlands and Shield to the north. Agricultural soils generally occupy the lowlands, especially the Saint-Lawrence River lowlands and the Lake Saint-Jean area (Lajoie 1975). In the highlands, there is a large variety of parent materials, but podzolization is the main soil-forming process under well to moderately well drained conditions (National Atlas of Canada 1974). This process is favored by the excess of precipitation over evapotranspiration, ranging from 500 to 900 mm annually (Fig. 1).

The degree of development of Podzolic soils varies considerably, as does the susceptibility of acidification or acid solutions. The objectives of this presentation are to analyze some characteristics of typical soil profiles, to summarize the processes that control the development of Podzolic soils, and to evaluate possible effects of an additional load of protons on their evolution.

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*Contribution No. 219, Sainte-Foy Research Station.

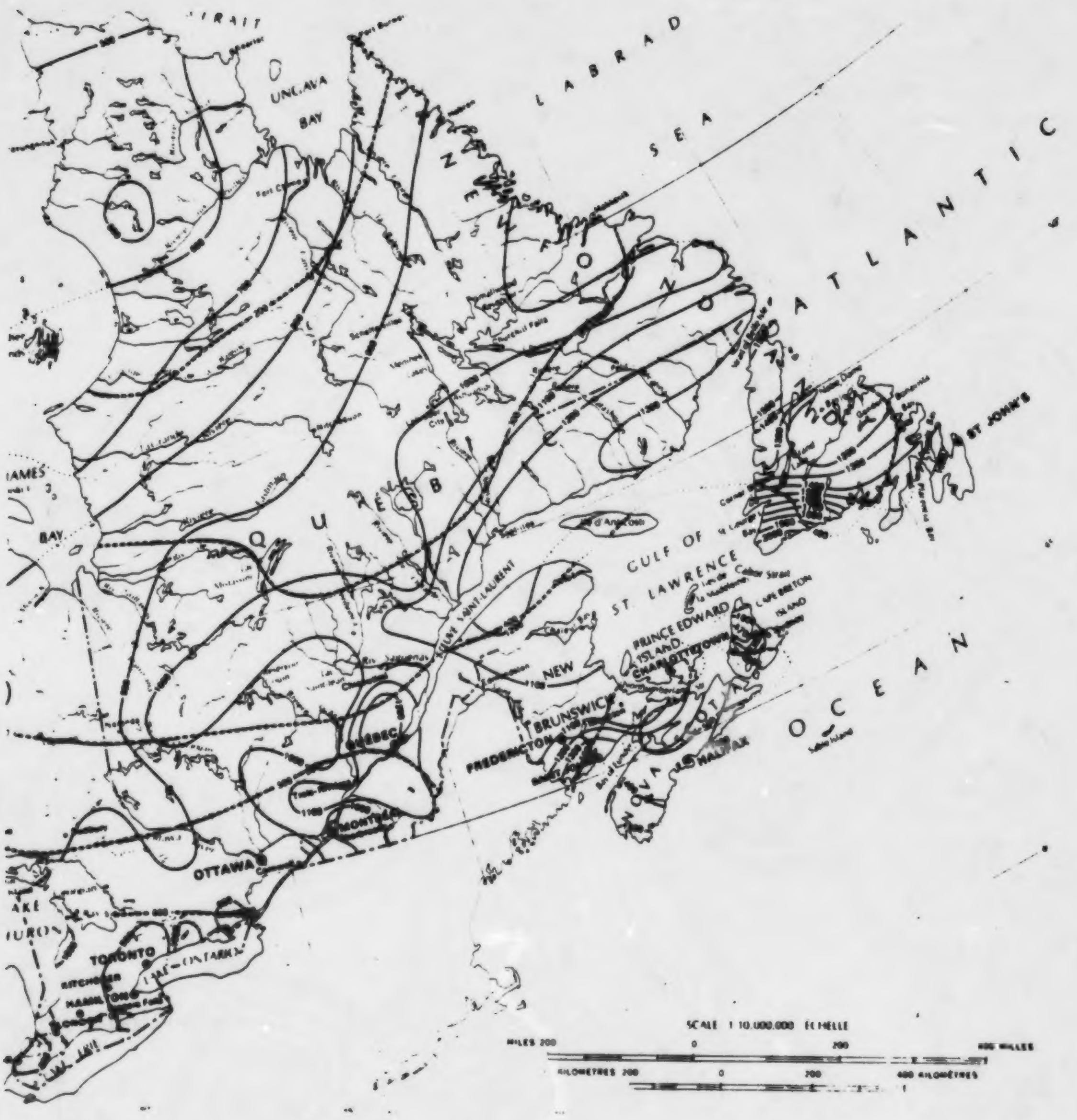
LABRAD
SEA
UNGAVA BAY
ATLANTIC
OCEAN
QUEBEC
JAMES BAY
GULF OF ST LAWRENCE
FLEUVE SAINT-LAURENT
Île d'Anticosti
Cabot Strait
PRINCE EDWARD ISLAND
CHARLOTTETOWN
CAPE BRETON ISLAND
NEW BRUNSWICK
FREDERICTON
HALIFAX
NOVA SCOTIA
ST JOHN'S
QUEBEC
MONTREAL
OTTAWA
TORONTO
KITCHENER
HAMILTON
LAKE ONTARIO
LAKE HURON
SCALE 1:10,000,000 ÉCHELLE
MILES 200 0 200 400 MILLES
KILOMETRES 200 0 200 400 KILOMÈTRES

Figure 1. Map showing the annual precipitation (full line) and evapotranspiration (dotted line) in eastern Canada. (From: Hydrological Atlas of Canada 1978).

SOIL CHARACTERISTICS

Till is the parent material for most soils, and, in the Appalachian Highlands, it is derived from more or less weathered schists, slates, shales, sandstones and limestone. The texture is sandy clay loam or coarser, and the reaction ranges from slightly acid to moderately alkaline. The presence of limestone or various basic and ultrabasic minerals in the till has a retarding effect on podzolization, because they supply considerable amounts of cations. The B horizons may contain large percentages of pyrophosphate-extractable sesquioxides that have been transported from the Ae horizon, but, on the other hand, an extensive disaggregation of the material that results in high clay content is the reason why many horizons do not meet one of the criteria for the Podzolic B horizon classification, namely a *(Fe + Al) pyro (in %)* / Clay (in %) ratio $\geq$ 0.05 (Canadian Soil Survey Committee 1978). The equivalent requirement in the U.S. classification for a Spodic horizon is a ratio of at least 0.20 (Soil Survey Staff 1975). In most soils under good drainage conditions, however, leaching of bases is appreciable, and the solum becomes acid.

These observations may be illustrated by a few examples. In a soil developed on calcareous till (Table 1, Esprit-Saint profile), the solum is completely depleted of carbonates, and there is an abrupt change in the soil reaction at the contact with the carbonate-rich horizon at a depth of 28 cm. In the B horizons, pyrophosphate-extractable (Fe + Al) content varies from 1.0 to 1.2%, but, on the other hand, the clay percentage is high and the sesquioxide / clay ratio is lower than 0.05. Nevertheless, this profile demonstrates the intensity of leaching and related acidification. A different situation is observed near Mount Orford, east of Montreal, in a profile developed on a metabasalt saprolite (Table 2). Leaching of bases is slower than in limestone, and the profile is slightly less acid. Pyrophosphate-extractable (Fe + Al) content varies from 1.0 to 1.4%, and some horizons meet the requirement of a Podzolic B horizon (De Kimpe et al. 1983b), because of a lesser disaggregation of the parent material and a clay content of only 14%. The most common parent material in the Appalachian Highlands is a neutral to slightly calcareous till. The soil profiles on such materials present all the features of a typical Podzolic soil (Table 1, Arago profile), and sometimes the B horizons also meet the Spodic horizon criteria.

In the Laurentian Highlands, the parent material is different by nature and texture. In the western part of the province, some soils have developed from till derived from dolomitic material. Dolomite dissolves more slowly than calcite and Brunisolic soils occur frequently. In most of the area, however, the till is derived from granite and gneiss. It is coarse, acid, compact and has a low permeability. This type of till supports Podzolic soils that commonly meet the Podzolic and Spodic B horizon criteria, like the Laurentide profile (Table 1, lower profile) characterized by large amounts of pyrophosphate-extractable sesquioxides, from 1.5% in the Bf_2 to 5.8% in the Bhf_2 horizons, and with clay contents less than 10%.

PODZOLIZATION MECHANISMS

The principal factors controlling the development of Podzolic soils are the leaching of bases and the translocation of Al^{3+} and Fe^{3+} ions released from mineral structures by weathering to the B horizons.

Table 1. Selected soil properties for three profiles developed on various parent materials

Horizon	Depth (cm)	pH (0.01 M $CaCl_2$)	Sand (%)	Clay (%)	$CaCO_3$ (%)	OM (%)	Fe[4]			Al[4]		
							d (%)	o (%)	p (%)	d (%)	o (%)	p (%)
Soil profile on a calcareous till, Esprit-Saint, Rimouski County, Appalachian Highlands[1]												
Ae	0-5	5.2	4.0	34.0	—	2.1	2.4	0.8	0.6	0.2	0.1	0.1
Bt_1	5-10	4.6	6.0	43.0	—	2.3	2.9	1.0	0.9	0.4	0.4	0.3
Bt_2	10-18	4.6	3.0	41.0	—	1.9	3.2	0.9	0.8	0.4	0.3	0.2
Bt_3	18-28	4.7	2.0	42.0	—	1.5	3.4	0.8	0.8	0.4	0.3	0.2
BC	28-35	7.0	7.0	19.0	48	0.6	1.9	0.3	0.1	0.1	0.1	tr
Rk	35	7.4	5.0	13.0	66	tr	1.1	0.2	tr	tr	tr	tr
Arago series, on a slightly calcareous till, Saint-Marcel, L'Islet County, Appalachian Highlands[2]												
Ae	0-10	3.6	50.0	9.0	—	0.5	0.4	0.1	0.1	tr	0.1	tr
Bhf	10-20	4.5	34.0	25.0	—	5.8	2.3	1.7	1.1	1.8	2.2	1.4
Bf	20-30	4.6	45.0	26.0	—	2.1	1.0	0.5	0.3	0.7	0.9	0.5
Aex	30-37	4.7	49.0	15.0	—	0.6	1.0	0.4	0.3	0.3	0.4	0.3
Btx_1	37-90	5.3	47.0	23.0	—	0.2	1.1	0.4	0.1	0.1	0.1	0.1
Btx_2	90-180	5.9	49.0	21.0	—	—	1.3	0.5	tr	0.1	0.1	tr
Btx_3	180-240	6.1	51.0	19.0	—	—	1.3	0.4	—	0.1	0.1	—
C	240	7.5	52.0	13.0	1.8	—	1.3	0.3	—	0.1	0.1	—
Laurentide profile, on an acidic till, Montmorency Forest, Laurentian Highlands[3]												
Ae	0-5	3.5	79.0	1.0	—	1.2	tr	0.1	tr	tr	tr	tr
Bhf_1	5-11	3.6	72.0	7.0	—	15.7	3.5	3.6	3.3	1.4	1.1	1.5
Bhf_2	11-17	4.1	72.0	9.0	—	13.8	3.0	2.8	2.4	3.5	2.8	3.4
Bf_1	17-27	4.2	78.0	5.0	—	6.6	2.1	1.9	1.5	3.0	2.4	2.8
Bf_2	27-40	4.3	68.0	5.0	—	2.8	1.2	1.0	0.6	1.6	1.5	0.9
BC	40-56	4.3	71.0	2.0	—	1.0	0.8	0.6	0.2	0.6	1.0	0.6
C	56-120	4.7	80.0	2.0	—	0.9	0.5	0.5	tr	0.3	0.5	0.2

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[1] Adapted from Laflamme et al. (1973)

[2] Adapted from De Kimpe et al. (1976)

[3] Adapted from Bourbeau and Gonzalez (1973)

[4] d: dithionite-citrate-bicarbonate; o: oxalate; p: pyrophosphate

Table 2. Soil profile on a metabasalt saprolite, near Mount Orford, Brome County, Quebec[1]

Selected soil properties

Horizon	Depth (cm)	pH (H_2O)	Sand (%)	Clay (%)	$CaCO_3$ (%)	OM (%)	Fe[2]			Al[2]		
							d (%)	o (%)	p (%)	d (%)	o (%)	p (%)
Ae	0-5	4.8	15.0	12.0	—	11.6	1.7	1.6	1.0	0.4	0.5	0.4
Bm_1-Bfj	5-25	5.0	26.0	14.0	—	2.4	1.8	1.4	0.6	0.8	1.1	0.8
Bm_2Bfj	25-70	5.2	29.0	13.0	—	1.3	1.7	1.3	0.5	0.6	0.8	0.5
BC	70-90	5.7	26.0	13.0	—	0.6	1.1	1.0	0.2	0.3	0.4	0.2
C	90-120	6.0	31.0	10.0	—	0.4	0.9	0.9	0.2	0.2	0.3	0.1

Total chemical analysis (less than 2 mm soil)

Horizon	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	H_2O
	%										
Ah	47.1	16.2	12.5	tr	1.8	0.3	4.6	7.0	0.3	3.7	5.3
Bm_1-Bfj	48.2	18.5	0.3	10.9	1.9	0.3	4.8	8.1	0.4	3.8	2.8
Bm_2-Bfj	49.0	18.2	2.8	8.5	1.8	0.3	4.5	8.3	0.3	4.1	2.3
BC	47.0	18.3	1.0	10.3	1.9	0.2	5.1	9.6	0.2	4.0	1.9
C	46.2	18.3	0.2	11.2	1.9	0.2	6.2	9.5	0.2	4.0	1.5

[1] From De Kimpe et al. (1983b)

[2] d: dithionite-citrate-bicarbonate; o: oxalate; p: pyrophosphate

Under the prevailing pH conditions, there is no restriction on the movement of ions such as Ca^{2+}, Mg^{2+}, Na^+ or K^+ (Fig. 2), except for a possible retention of some Mg^{2+} and K^+ in secondary mineral structures or on exchange sites, as shown later. The situation is different for Fe^{3+} and Al^{3+} ions: at about pH 4.5, Fe^{3+} is insoluble whereas Al^{3+} is nearly insoluble. A commonly accepted theory was that these ions, when released in the Ae horizon, were mobilized and translocated to the B horizons as organometallic complexes or chelates. Many authors studied the formation of such complexes. For the present discussion, it is appropriate to consider the results of a comparison between the effects of organic and mineral acids on the weathering of minerals. In these investigations, Robert and coworkers (Robert et al. 1979, 1980; Razzaghe and Robert 1979) determined the effects of two mineral acids and several low molecular weight organic acids on the dissolution of minerals and the complexation of Al. All acids were used at a low concentration ($\sim 10^{-3}$ N) and in open and closed systems to reproduce natural conditions as closely as possible. Three groups of acids were defined (Fig. 3). In the first, a few acids have combined acid and complexing properties. They can, therefore, extract considerable amounts of Al from the minerals because the formation of chelates removes ions from the solution (Huang and Keller 1972). The second group includes a number of organic acids and also the mineral acids that have acid properties only. Many humic and fulvic acids belong to this group. Aluminum extractability by these acids represents 20-30% of that obtained by the acids from the first group. Finally, in the third group, the acids are not very different from water in their ability to release Al from the mineral structures. The authors concluded that protons have the primary and essential role to break down the structures and to release the cations. The formation of complexes occurs at a subsequent stage, and involves Fe and Al ions already present in the solution. When complexation is present, extraction of the major cations follows the decreasing sequence: $Al^{3+} > Fe^{3+} > Mg^{2+} > Si^{4+}$, although in the absence of complexation, the sequence becomes $Mg^{2+} > Si^{4+} > Fe^{3+} > Al^{3+}$ (Robert and Veneau 1978).

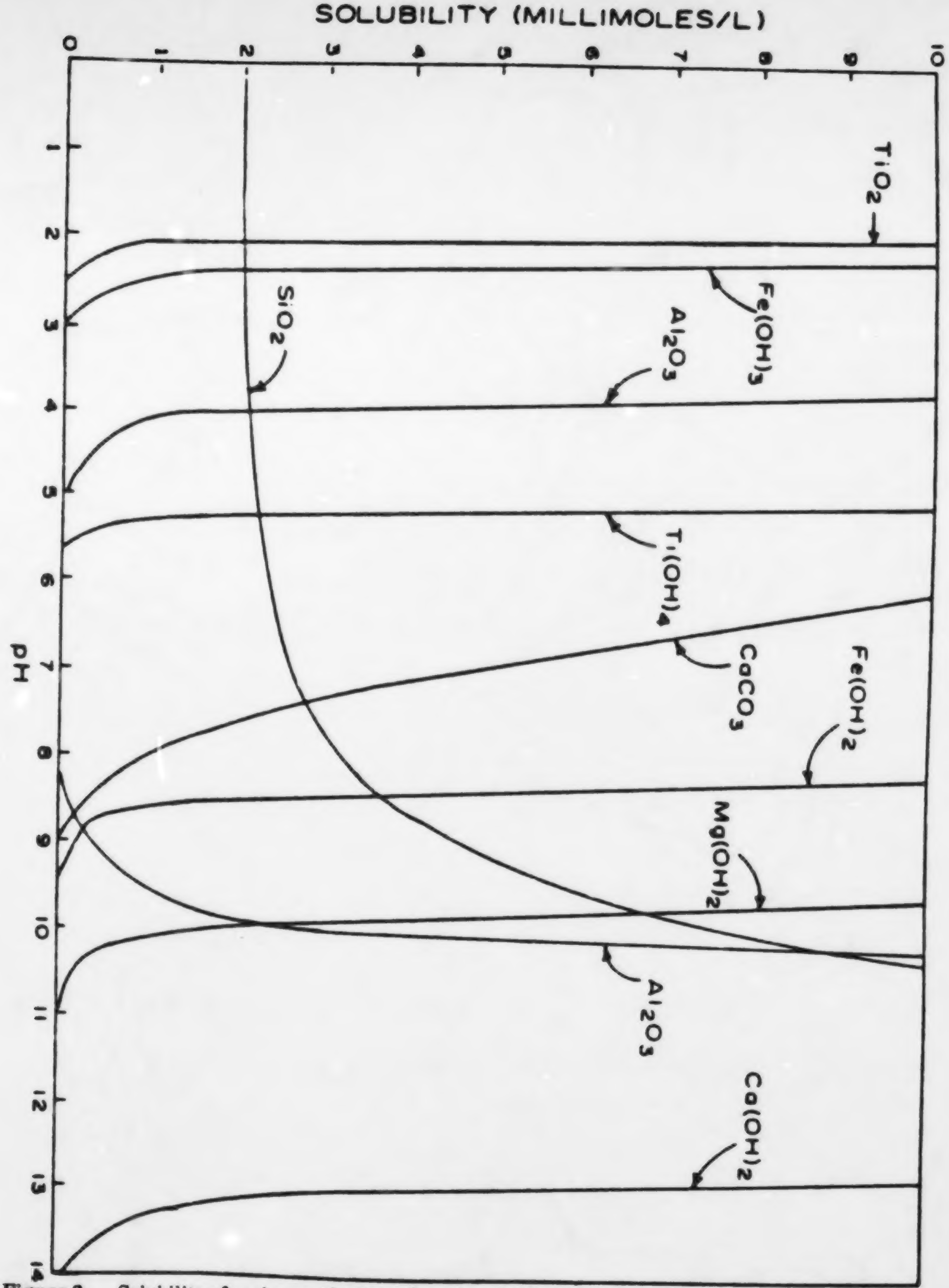


Figure 2. Solubility of various cations as a function of pH. (From: Loughnan 1969).

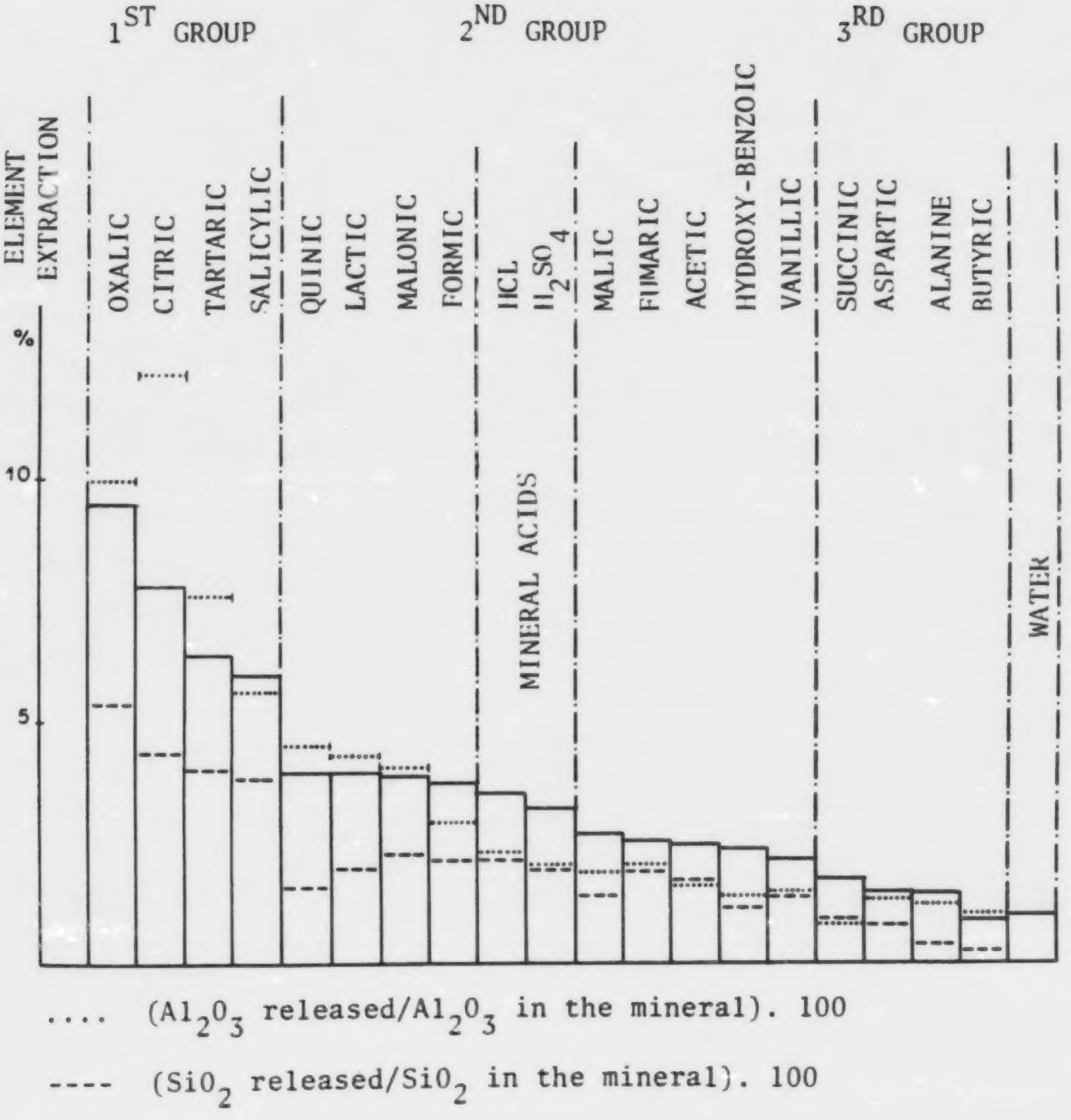


Figure 3. Dissolution of a phlogopite by various mineral and organic acids. (From: Robert et al. 1979).

These experiments support a differentiation among Podzolic soils formed under different types of vegetation, because the litter degradation produces different organic acids. In the Appalachian Highlands, under deciduous trees, the Ae horizon thickness for five Arago profiles ranged from 15 to 27 cm, while it was commonly less than 10 cm under conifers (De Kimpe, unpublished data). A similar observation was reported for sod-podzolic soils from the southern taiga regions of the USSR (Gerasimova 1981). Another effect of vegetation is a different distribution of Al and Fe in the Podzolic B horizons (De Kimpe and Martel 1976), which may be explained by the nature of the degradation products of humus under both types of vegetation (Robin et al. 1981).

The above theory, which considers the organometallic complexes as the main factor responsible for the formation of the Podzolic B horizons, cannot account satisfactorily for the formation of Bf or Bs horizons rich in allophane (Farmer 1982). The presence of imogolite and allophane in the lower part of the profiles (Brydon and Shimoda 1972) led Farmer and coworkers (Farmer et al. 1980; Anderson et al. 1982) to conclude that aluminum is transported to the deeper horizons as an aluminosilicate (protoimogolite) complex: in dilute acid solutions, at pH <5, hydroxyaluminum cations react with orthosilicic acid to form protoimogolite in which the Al/Si ratio is about 2. Such mineral complexes are very stable, much more than the corresponding Fe_2O_3 - SiO_2 - H_2O complexes, and they have the necessary colloidal stability to transport Al^{3+}, Si^{4+} and, to a lesser extent, Fe^{3+} ions in the Podzols. This process is particularly important to explain the mobility of Al^{3+} at pH values higher than the precipitation pH without the contribution of organic matter. Formation of protoimogolite requires the dissolution of Al- and Si-bearing minerals at an initial stage; this dissolution can be performed equally by organic and mineral acids.

In this "mineral theory of Podzolization", there is still a place for organometallic complexes. Fixation of organic molecules would be subsequent to the migration of the mineral complexes (Anderson et al. 1982). During periods of heavy rainfall, organic colloids migrate and combine with the mineral cations in the upper part of the B horizons where they coagulate. Pokojska (1979) determined that a $\underline{(\%C\ (FA_{1a,1} + HA_1))}$ / % free R_2O_3 ratio of 2 was the lower limit of mobility for the organometallic complexes. In the Ao and Ae horizons of Podzolic soils, this author determined a ratio value ranging from 31.9 to 2.1, which dropped to values between 1.8 and 0.1 in the Bh horizons where the complexes were immobilized. These observations are in line with the general distribution of organic matter in the Podzolic B horizons where the percentage rapidly decreases with depth. Some implications of the mineral theory of Podzolization in relation to acid loading are considered later.

SOIL MINERALOGY

Among all types of soils in Canada, Podzols exhibit the greatest degree of mineral weathering, followed, to a lesser degree, by Brunisols and Gleysols (Kodama 1979). Brunisolic soils, in particular, are often considered as evolving towards the Podzols, but they lack the minimum expression required to meet this order criterion. Furthermore, they frequently develop on materials less depleted of cations and, therefore, are less susceptible to acid weathering.

Mineralogical transformations must be considered in each particular environment. In the Canadian Shield and Laurentian Highlands subsoils, derived from granite and gneiss, the main primary minerals are quartz, feldspars, amphiboles and pyroxenes. Micas are the most abundant phyllosilicates, followed in decreasing order by mixed-layer minerals, vermiculite, smectite and some chlorite plus kaolinite. In the Appalachian Highlands, the phyllosilicate occurrence frequency in the subsoils indicates micas as dominant, followed by chlorite and some kaolinite (Kodama 1979). From the point of view of mineral transformations, two types of Podzolic soils are found in Quebec:

type (1): is characterized by a complete or nearly complete disappearance of chlorite from the Ae horizon and an enhancement of swelling clay minerals in the same horizons, type (2): is characterized by the presence of noticeable amounts of inherited chlorite and also by the enhancement of swelling minerals.

The second type is generally associated with a lesser degree of maturity of the soils; it is more commonly observed in the Podzolic soils of the lowlands.

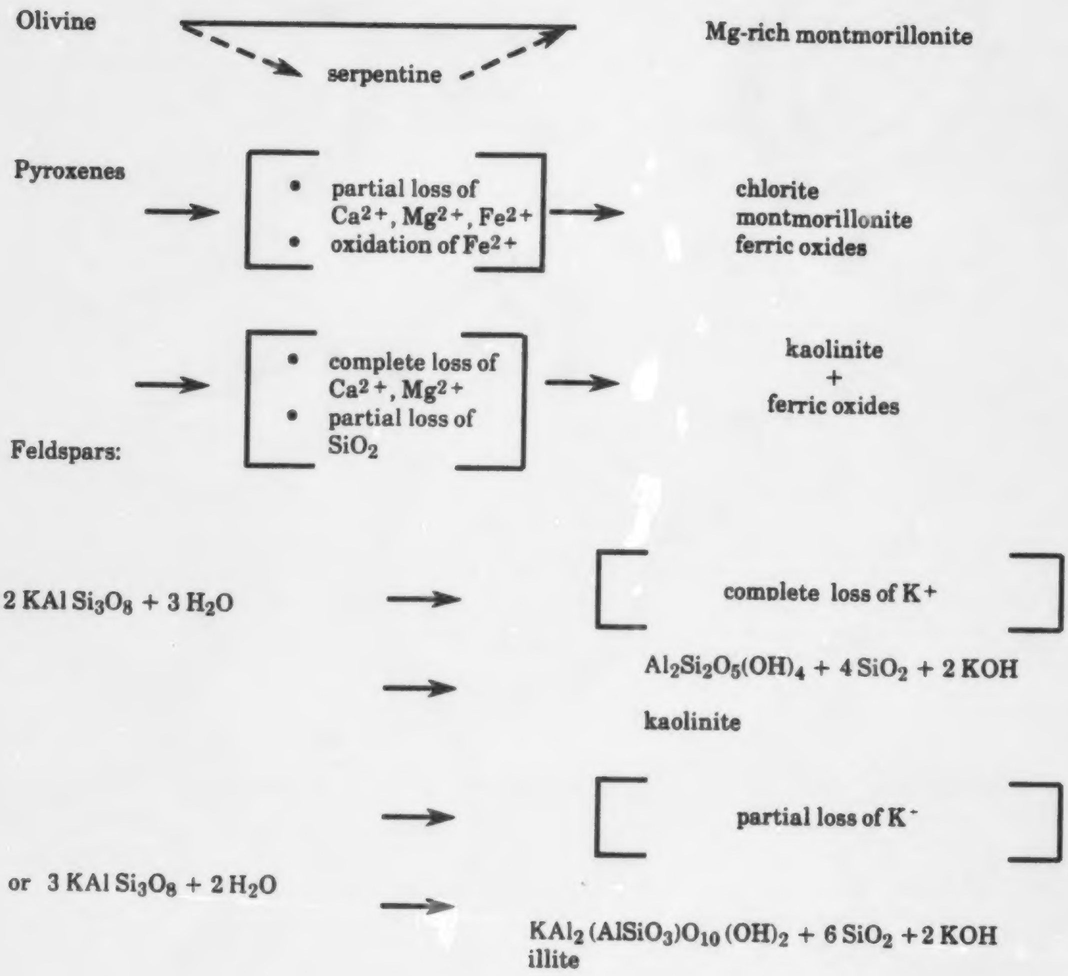
Under acid weathering, chlorites are decomposed and the cations are transported to the B horizons where they contribute to the formation of secondary minerals, either single species such as vermiculite or as mixed-layer structures, vermiculite-chlorite or smectite-chlorite. When illites and other micas are depleted of their interlayer K^+, they transform into expanding clay minerals, especially smectite in the Ae horizon (Brydon et al. 1968). Under intense leaching and low pH conditions, kaolinite, one of the simplest clay minerals with the composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, would be expected to be the ultimate product of weathering. This hypothesis has been tested in six well-developed profiles from the Laurentian Highlands. In four of these profiles, kaolinite was present in trace amounts only. In the other two profiles, kaolinite content showed a maximum in the Ae horizon (Table 3). However, in profile 5, a second maximum was also observed in the C horizon. This observation casts some doubt on the preferential formation of this clay mineral in the Ae horizon. Another hypothesis considers kaolinite as a residual mineral incorporated into the till during the Wisconsinian ice period. The occurrence of old saprolites with high percentages of kaolinite supports this hypothesis.

The content of primary minerals, feldspars, pyroxenes and amphiboles generally decreases towards the surface in Podzolic soils, although quartz content is commonly highest in the Ae horizon. Alteration of primary minerals is initiated by a cation depletion that results from an H^+/Ca^{+2}, Mg^{+2} substitution (Schott et al. 1981). Various secondary minerals can be produced as indicated by the following reactions for a few minerals:

Table 3. Kaolinite content in two Sainte-Agathe profiles[1]

	Horizon	Kaolinite content (%)
Profile 1	LFH	1.0
	Ah (Ae)	0.8
	Ae	1.4
	Bf_1	0.7
	Bf_2	0.3
	BC	0
	C	0
Profile 9	LFH	1.5
	Ae	4.0
	Bhf	3.0
	Bf	1.7
	C	5.1

[1] From C.R. De Kimpe, and N. Miles, unpublished data


Olivine
Mg-rich montmorillonite
serpentine
Pyroxenes
partial loss of Ca^{2+}, Mg^{2+}, Fe^{2+}
oxidation of Fe^{2+}
chlorite
montmorillonite
ferric oxides
complete loss of Ca^{2+}, Mg^{2+}
partial loss of SiO_2
kaolinite + ferric oxides
Feldspars:
$2\,KAl\,Si_3O_8 + 3\,H_2O$
complete loss of K^+
$Al_2Si_2O_5(OH)_4 + 4\,SiO_2 + 2\,KOH$
kaolinite
partial loss of K^+
or $3\,KAl\,Si_3O_8 + 2\,H_2O$
$KAl_2(AlSiO_3)O_{10}(OH)_2 + 6\,SiO_2 + 2\,KOH$
illite

These reactions indicate that the final product depends considerably on the degree of leaching of Ca^{2+}, Mg^{2+}, and K^+ cations from the profile, and on the Al_2O_3/SiO_2 relative ratio (Wilson 1975).

ACIDIFICATION AND SOIL EVOLUTION

In Podzolic soils, residual primary minerals such as feldspar and hornblende, although decreasing towards the surface, are frequently reported even in the fine fraction of the solum; smectite is the common degradation product in the Ae horizon. This mineral assemblage indicates that the Podzolic soils of Quebec have not reached the ultimate stage of weathering and that they still have some potential for H^+ ion neutralization. There are several implications thereby arising. Two main factors determine the neutralization ability of a soil: the availability of cations and the residence time of the solution percolating through the soil.

Availability of cations is extremely variable throughout a profile. It depends on the percentage and the particle size, hence the surface area of weatherable primary minerals; and on the nature, the specific surface area and the cation exchange capacity of the secondary minerals. Base saturation in the solum generally ranges from 40 to 60% of the exchange capacity, although it reaches 100% in the parent material. The clay content may vary between 15 and 40% in the Appalachian Highlands Podzolic soils, although it is commonly less than 15% in the Laurentian Highlands soils. A wide range in cation availability can thus be expected. Experimental studies on the weathering of amphibole and pyroxene (Schott et al. 1981; Berner and Schott 1982) showed that the H^+/cation exchange proceeds very rapidly. For three profiles developed on metabasalt and similar to the one presented earlier (Table 2), significant relations were obtained between the pH values measured after 30-minute contact in a 1:1 soil:water mixture and the total CaO ($r = 0.748^{**}$), CaO + MgO ($r = 0.877^{**}$) and CaO + MgO + Na_2O ($r = 0.811^{**}$) percentages determined from total chemical analysis (De Kimpe et al. 1983b). These pH values (Table 2) were below abrasion pH values which, for minerals containing M^+ and M^{2+} ions, would be expected to be alkaline (Stevens and Carron 1948; Grant 1969). Yet, the relations demonstrate the ability of the soil to release cations and neutralize the protons when the texture of the material is fine enough. In Podzolic soils, however, the development of Ae horizons reduces the amount of available cations in the solum. Swelling minerals with a CEC value above 100 meq 100 g^{-1} of clay can retain some Ca^{2+} and Mg^{2+} ions for H^+ neutralization, but when completely depleted of exchangeable base cations, which are replaced by Al^{3+} and H^+, smectite also becomes susceptible to hydrolysis.

The second main factor influencing acid neutralization is the residence time of water in the soil, especially in the horizons which supply the largest amounts of cation. Saturated hydraulic conductivity has been measured in some profiles (Mehuys and De Kimpe 1976), and the values generally decreased considerably at the contact between the solum and the parent material, as an inverse function of bulk density (Fig. 4). This results in abundant seepage at that level in the spring and the fall. More water is circulating in the solum, where water residence time and available cation contents are lower than at depth: consequently, the electrolyte concentration in the water percolating in the solum is lower than in deep running water. Electrolyte concentration measurements near Lake Laflamme, Montmorency Forest, confirmed this observation. In water collected from low-depth piezometers (less than 1 m), the (Ca^{2+}, Mg^{2+}, Na^+, K^+) concentration ranged from 0.2 to 0.4 meq L^{-1}, while in water collected from deep piezometers (over 10 m), the cation content varied between 0.6 and 0.75 meq/L^{-1} (L.M. Azzaria, personal communication, 1983). In the latter case, residence time of water in the soil was longer, and water moved through base-saturated material. A low electrolyte content was also in agreement with the data of Shilts (1981) concerning the sensitivity of bedrock and derived soils to acid precipitation in southeastern Canada.

Finally, another effect of soil acidification is a contribution of aluminosilicate conplexes to subsoil cementation. Migration of these complexes to the lower B horizons, as proposed by Farmer et al. (1980), may favor the formation of less permeable horizons. Intergrade duric-fragic horizons have been described in several Podzolic soils of Quebec (Pagé et al. 1979), and the presence of aluminosilicate complexes may add to the induration of the fragic horizons (De Kimpe et al. 1983a) and also to a further decrease in the amount of water percolating through the subsoil.

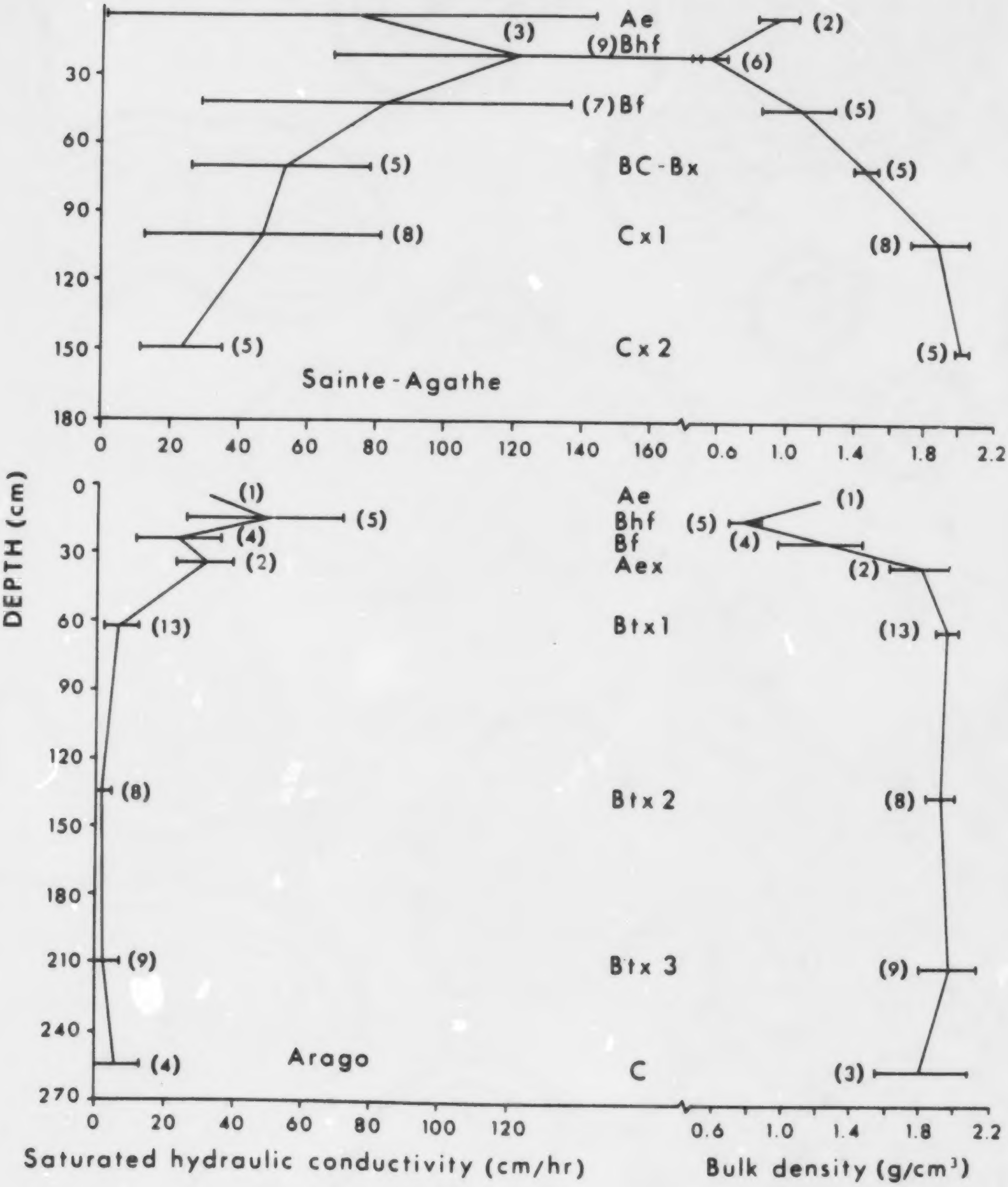


Figure 4. Saturated hydraulic conductivity and bulk density for the various horizons of Laurentian (Sainte-Agathe) and Appalachian (Arago) Podzolic soils. (From: Mehuys and De Kimpe 1976).

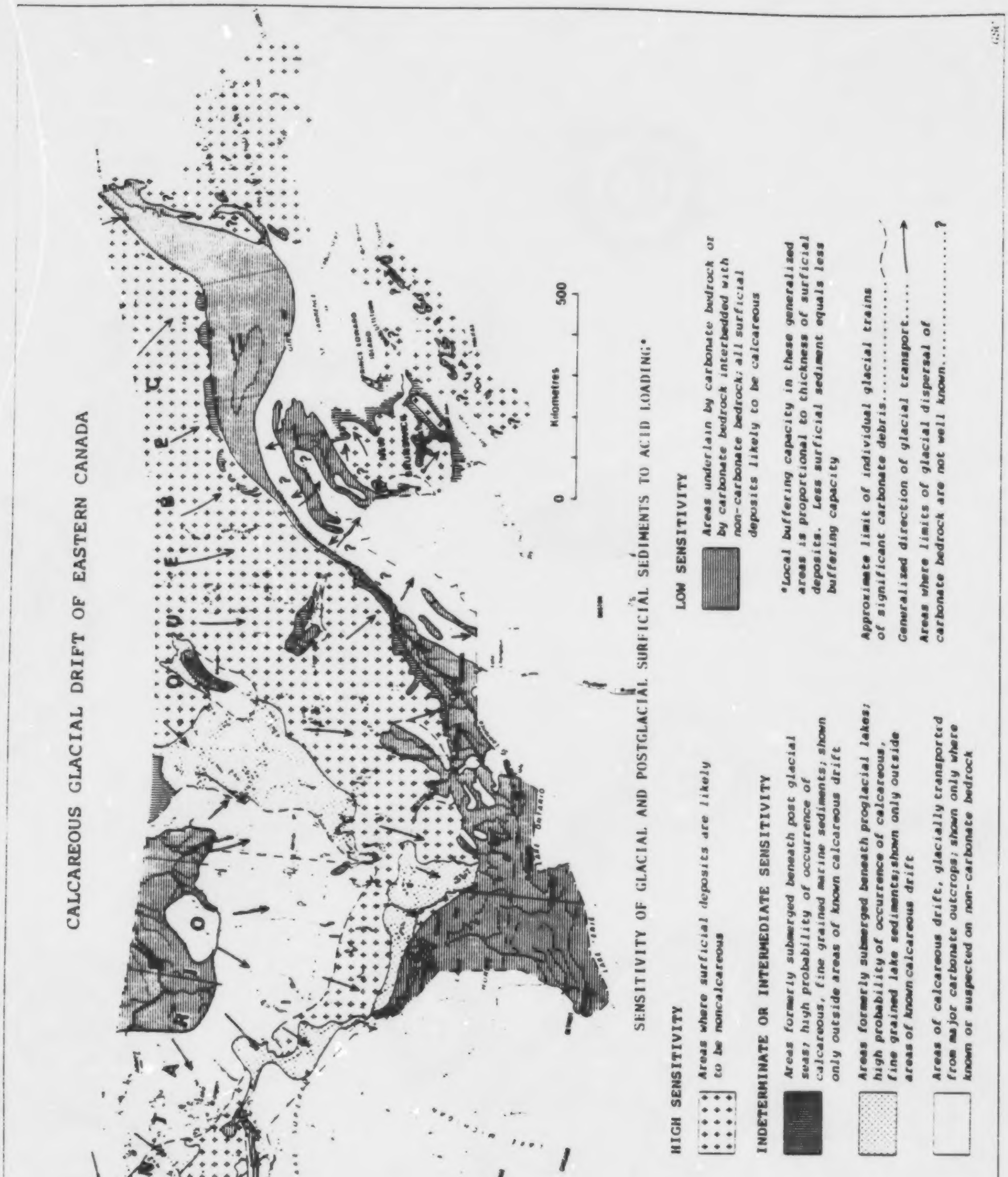

CALCAREOUS GLACIAL DRIFT OF EASTERN CANADA
ONTARIO
QUEBEC
PRINCE EDWARD ISLAND
NEW BRUNSWICK
LAKE ONTARIO
LAKE ERIE
0
Kilometres
500
SENSITIVITY OF GLACIAL AND POSTGLACIAL SURFICIAL SEDIMENTS TO ACID LOADING*
HIGH SENSITIVITY
Areas where surficial deposits are likely to be noncalcareous
INDETERMINATE OR INTERMEDIATE SENSITIVITY
Areas formerly submerged beneath post glacial seas; high probability of occurrence of calcareous, fine grained marine sediments; shown only outside areas of known calcareous drift
Areas formerly submerged beneath proglacial lakes; high probability of occurrence of calcareous, fine grained lake sediments; shown only outside areas of known calcareous drift
Areas of calcareous drift, glacially transported from major carbonate outcrops; shown only where known or suspected on non-carbonate bedrock
LOW SENSITIVITY
Areas underlain by carbonate bedrock or by carbonate bedrock interbedded with non-carbonate bedrock; all surficial deposits likely to be calcareous
*Local buffering capacity in these generalized areas is proportional to thickness of surficial deposits. Less surficial sediment equals less buffering capacity
Approximate limit of individual glacial trains of significant carbonate debris
Generalized direction of glacial transport
Areas where limits of glacial dispersal of carbonate bedrock are not well known ?
GSC

Figure 5. Sensitivity of glacial and postglacial surficial sediments to acid loading. (From: Shilts 1981).

CONCLUSIONS

Podzolization is a natural process that results in a strong acidification of the solum and a depletion of bases and nutrients (Haman 1977). Important processes controlling the development of Podzolic soils are the dissolution of primary minerals and the leaching of bases.

The mobility of Al and Si exceeds what was generally thought because mineral aluminosilicate complexes such as protoimogolite are less subject to immobilization than the organometallic complexes (Farmer 1982).

It has been calculated (Bache 1983) that the complete transformation of 1 m^3 of granite into kaolinite and soluble silica can neutralize 9 keq of H^+ ions. This figure or a value close to it might also be applied to unweathered till in the Laurentian Highlands and certainly in the Appalachian Highlands. In deep till soils, there is a high potential for acid neutralization, but its effectiveness is considerably reduced by the limited accessibility of the lower horizons to percolating waters.

Under natural conditions, Podzolic soils may be expected to reach an equilibrium, but it is very difficult to predict their evolution in the presence of an additional load of H^+ ions coming from acid precipitation.

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TECHNICAL SESSION VI
IMPLICATIONS OF ACID RAIN FOR FOREST ECOSYSTEMS

Acid Deposition and Element Cycling in Eastern North American Forests

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ABSTRACT

Current knowledge of the relationship between atmospheric deposition of acids and acid-forming substances on the one hand and element fluxes on the other in major eastern North American forest types is reviewed. A mature tolerant hardwood forest on a well-drained acid till soil at Turkey Lakes Watershed in northern Ontario serves as a point of reference. Nitrogen (N) and sulphur (S) fluxes between element pools within the ecosystem are emphasized because of the association of N- and S- forms with acid pollution. Nitrogen turnover (ca. 45 kg ha^{-1} yr^{-1}) in the reference forest ecosystem is much greater than atmospheric N input (ca. 12 kg ha^{-1} yr^{-1}) and streamflow N output (ca. 7 kg ha^{-1} yr^{-1}). Thus, a tight cycle of N is maintained in this undisturbed old-growth hardwood forest. Input/output of sulphate-S (SO_4-S) in the watershed is roughly in balance. Sulphate concentrations are equal to 70% of the total base cation concentrations, on an equivalent-weight basis, in soil water below the rooting zone of the reference forest. At current levels, atmospheric inputs of SO_4-S contribute significantly to losses of base cations (potassium (K), calcium (Ca), magnesium (Mg), and sodium (Na)) from the rooting zone of many eastern ecosystems. A reduction in the quantity of SO_4-S entering eastern forest soils would likely reduce cation losses from these ecosystems.

INTRODUCTION

In a natural forest ecosystem the cycle of elements between soil and vegetation maintains the chemical composition of the soil solution in a favorable state for meeting the nutrient requirements of a productive forest. The basics of a bioelement cycle are: input to the ecosystem from the atmosphere and mineral weathering; uptake from soil by trees and other vegetation; and transfer from trees to soil by a variety of processes including litterfall, canopy leaching by precipitation, root slough, and output from the tree rooting zone associated mainly with soil leaching. Ecosystem nutrient reserves are enhanced when atmospheric inputs are incorporated into the cycle and outputs from the tree rooting zone are minimized.

In the past decade there has been an increasing awareness of the magnitude of strong acid deposition in eastern North American forests. Along with this awareness there is concern that acid precipitation may alter nutrient cycles in such a way that soil and soil water may become more acid and, therefore, less favorable for forest growth. For example, an increase in the acidity of soil water could reduce the availability of nitrogen (N), phosphorus (P), and base cations (potassium (K), calcium (Ca), magnesium (Mg), and sodium Na) and could increase the solubility of trace metals such as manganese (Mn) and aluminum (Al).

The objective of this paper is to review current knowledge of the relationship between atmospheric deposition of acids and element fluxes in major eastern North American forests. Nitrogen and sulphur (S) are emphasized because of the association of forms of these elements with acid pollution. A mature tolerant hardwood forest on a well-drained acid till soil in northern Ontario serves as a point of reference. The forest is located in the Turkey Lakes Watershed (lat. 47°03'N; long. 84°25'W), a field research site maintained by the Canadian Forestry Service and other agencies conducting acid rain studies. The data relate to a 7-ha sub-basin Watershed 31, supporting an old-growth sugar maple (*Acer saccharum* Marsh.) -yellow birch (*Betula alleghaniensis* Britton) forest with a basal area of 28.6 m^2 ha^{-1}, 82% of which was maple with dominants 120 to 180 years old. Soils are

Orthic Humo-Ferric and Ferro-Humic Podzols (Typic Haplorthods), derived from basalt and granite. In addition to the Turkey Lakes data, information on forest nutrient cycles from the following locations was incorporated into this review: Experimental Lakes Area (ELA), Orient Bay and Dorset, in Ontario; Huntington Forest, New York; Hubbard Brook, and Mount Moosilauke, New Hampshire; Coweeta, North Carolina; and Walker Branch, Tennessee (Fig. 1).

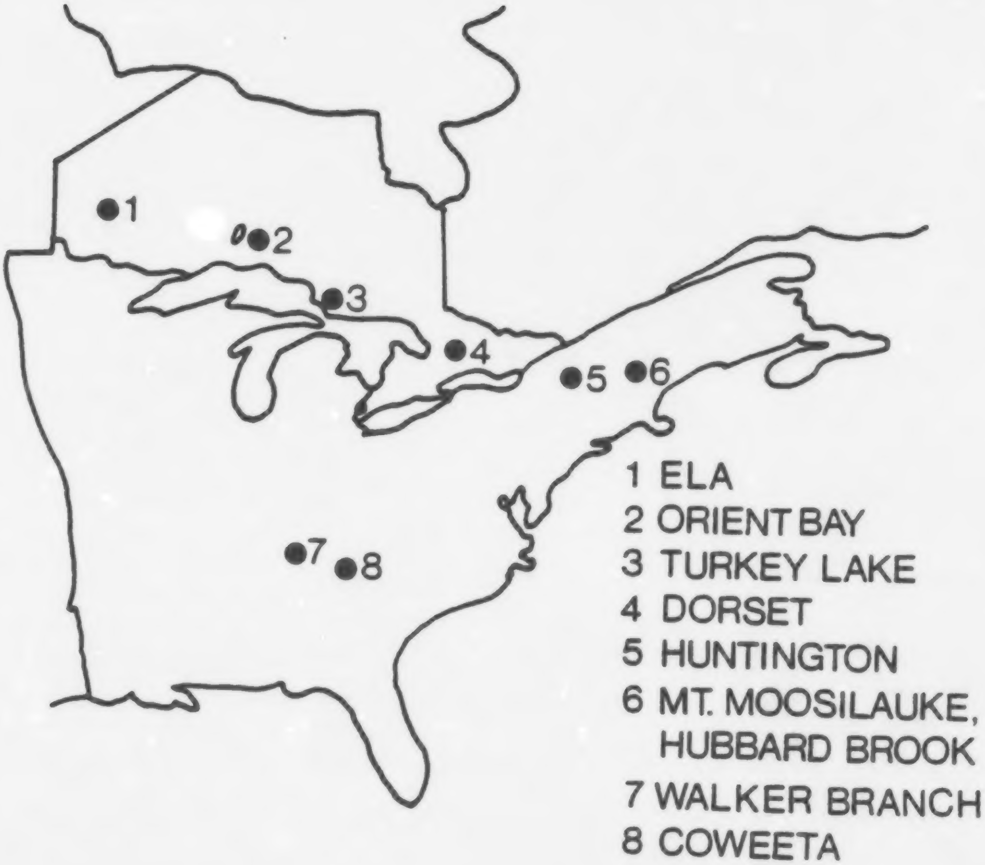
INPUTS

Comparisons with Alaska, which is remote from industrial activity, and Solling, West Germany, which is near a region of high industrial activity, are useful in our attempts to put into perspective the deposition of strong acids on eastern North American watersheds (Table 1). The concentrations of hydrogen (H), sulphate (SO_4), and nitrate (NO_3) in bulk precipitation measured in eastern forests are well above those reported for Alaska. Within eastern North America, for example, concentrations tended to increase eastward and southward from the Ontario-Manitoba border. From southern Ontario to New Hampshire, H concentrations approach those at Solling, although SO_4 and NO_3 concentrations are considerably less. Actual deposition, however, depends on the quantity as well as the composition of precipitation. Within eastern North America the deposition of strong acids is highest at high elevations in New Hampshire (2400 mm precipitation) and lowest in northwestern Ontario (700 mm precipitation). To determine if and how current atmospheric loadings of strong acids influence nutrient cycling, it is necessary to compare inputs with both the natural production and the retention of these acids within the ecosystem.

NITROGEN CYCLE

Total N in the reference ecosystem exceeds 10000 kg ha^{-1}. Most of this N is contained in organic matter associated with mineral soil to a depth of 50 cm, and in the forest floor (Fig. 2). The third largest pool is that in the living forest vegetation. Total N uptake by the tolerant hardwood reference is estimated according to Morrison (1984). A minimum of 45 kg N ha^{-1} yr^{-1} is required for growth by the forest, according to our estimates of annual uptake. Approximately 43 kg of N was mineralized in L and F horizons in 1981, an estimate determined by input output differences. (N mineralization rates as high as 60 kg ha^{-1} yr^{-1} may be realized in L and F horizons under the optimal temperature and moisture conditions of a laboratory experiment.) An annual transfer in litterfall of 40 kg ha^{-1} of N provides the source for N mineralized in the forest floor. Nitrogen turnover in the forest floor is supplemented by N mineralized from the large N reserves of mineral horizons, N in precipitation (ca. 12 kg ha^{-1} yr^{-1}), and N leached from the canopy (ca. 1 kg ha^{-1} yr^{-1}). Eighty percent of meteoric N input to the watershed is mineral N (i.e., ammonium (NH_4) and NO_3 ions) directly available for plant uptake. As precipitation inputs of N exceed streamflow outputs, N appears to be accumulating in the ecosystem. The internal cycle of N, therefore, is considerably larger than amounts of N discharged from the watershed in streamflow. A tight cycle of N is maintained in this undisturbed ecosystem. In the absence of information on N fixation and denitrification, however, a complete N balance cannot be constructed.

Estimated annual N turnover in the reference watershed is slightly less than that determined for other eastern hardwood forests, but considerably greater than in a natural conifer forest (Table 2). Nitrogen transfers in our tolerant hardwood forest are noticeably less than those in a younger, similar forest at Hubbard Brook, New Hampshire. The average foliar N concentration for 15 sugar maple trees at Turkey Lakes was 2.13%. The 1981 foliar N concentration was within the range of minimum (1.75%) to optimum (2.80%) for sugar maple (Mitchell and Chandler 1939), and this suggests adequate N supplies in the soil of the reference forest.


1
2
3
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6
7
8
1 ELA
2 ORIENT BAY
3 TURKEY LAKE
4 DORSET
5 HUNTINGTON
6 MT. MOOSILAUKE, HUBBARD BROOK
7 WALKER BRANCH
8 COWEETA

Figure 1. Research sites in eastern North America.

Table 1. The concentration of strong acid ions (μeq L^{-1}) in bulk precipitation

Location	H	SO_4	NO_3	Reference
St. Petersburg, Alaska	3	10	-	Johnson 1981
ELA, Ont.	13	37	4	Schindler (pers. commun.)
Orient Bay, Ont.	4	62	13	Nicolson (unpubl.)
Turkey Lakes, Ont.	37	58	40	Foster and Nicolson 1984
Dorset, Ont.	73	62	-	Dillon et al. 1978
Huntington, N.Y.	63	55	24	Mollitor and Raynal 1982
Mount Moosilauke, N.H.	83	75	21	Cronan 1980
Hubbard Brook, N.H.	72	60	24	Likens et al. 1977
Solling, West Germany	83	142	47	Mayer and Ulrich 1976

Table 2. Nitrogen turnover (kg ha^{-1} yr^{-1}) in eastern North American forest ecosystems

	Process			
Forest	Canopy leaching	Litterfall	Uptake[a]	Reference
Pinus banksiana Lamb.	-2.8	20.5	21.5	Foster and Morrison 1976
Acer saccharum Marsh. *Betula alleghaniensis* Britton	1.5	40.1	45.0	Morrison 1984, Foster (unpubl.)
Acer saccharum *Betula alleghaniensis* *Fagus grandifolia* Ehrh.	2.8	54.2	66.7	Likens et al. 1977
Quercus spp. *Carya* spp. *Acer rubrum* L.	4	33	50	Henderson et al. 1978
Quercus spp. *Carya* spp.	3	39	57	Henderson et al. 1978

[a] Calculated according to Morrison (1984).

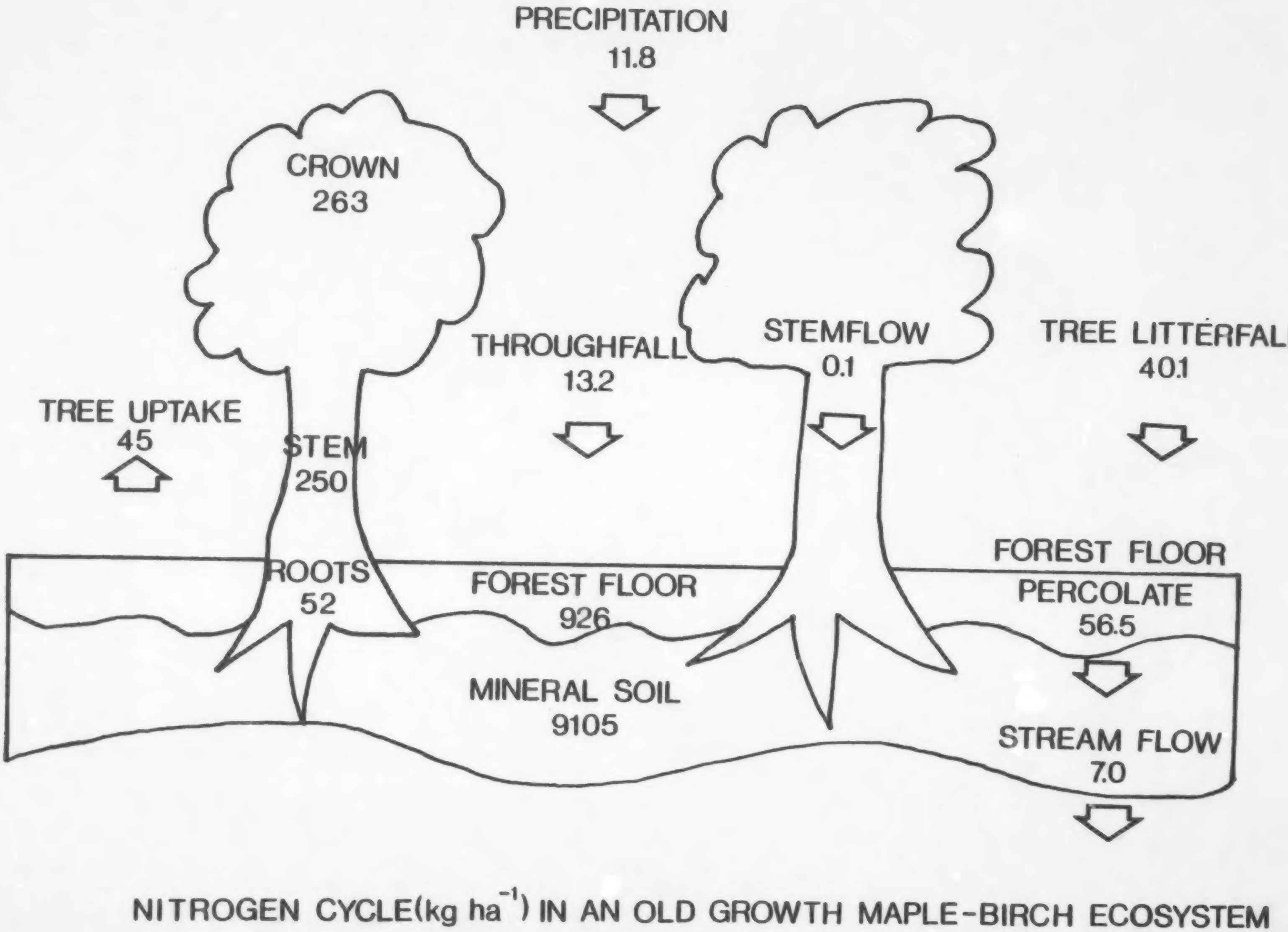
PRECIPITATION
11.8
CROWN
263
THROUGHFALL
13.2
STEMFLOW
0.1
TREE LITTERFALL
40.1
TREE UPTAKE
45
STEM
250
ROOTS
52
FOREST FLOOR
926
FOREST FLOOR
PERCOLATE
56.5
MINERAL SOIL
9105
STREAM FLOW
7.0
NITROGEN CYCLE(kg ha⁻¹) IN AN OLD GROWTH MAPLE-BIRCH ECOSYSTEM

Figure 2. The distribution and annual cycling of nitrogen (kg ha^{-1}) in an old-growth maple-birch ecosystem, Turkey Lakes Watershed.

Current eastern North American atmospheric loadings of nitrate-N (NO_3-N) are ca. 2 to 6 kg ha^{-1} yr^{-1}. We calculated that precipitation NO_3-N inputs would increase N availability in the reference hard wood soil by a minimum of 3% on the basis of a soil nitrification rate of 175 kg ha^{-1} yr^{-1}, determined under laboratory conditions (Van Loon and Rutherford 1983), or by a maximum of 13%, if we assume that uptake is an index of availability. Corresponding increases for a central Ontario jack pine (*Pinus banksiana* Lamb.) forest would be 21 and 23%, respectively. Greater annual N mineralization rates have generally been determined for hardwood than for conifer forests (Vitousek and Melillo 1979). Atmospheric NO_3-N, therefore, is more likely to benefit the productivity of conifer rather than hardwood forests because N is more often limited in conifer forests (Foster and Morrison 1983).

From simulation studies with the "JABOWA" model by Aber et al. (1982) it has been predicted that the growth of tolerant hardwoods will change in proportion to the supply of N. Conclusions concerning acid rain and forest productivity, however, are tentative. Waide and Swank (1977) caution that "conclusions from such simulation studies will depend on how element cycling models are conceptualized". Nitrogen cycling in a forest ecosystem is difficult to model because transport occurs in more than one phase, and because N transformations are regulated by biological processes that are controlled by physical parameters. It is not surprising, therefore, that N-cycle simulation models currently lack the sensitivity that would enable us to predict the extent to which forest ecosystem N cycles will be modified by acid precipitation. The ability to determine the sensitivity of forest nutrient cycles to disturbance will increase as our knowledge of ecosystem regulation processes improves.

As we have observed at Turkey Lakes, N inputs are consistently greater than outputs in other eastern North American forested watersheds (Table 3). Forests that receive large atmospheric deposition of NO_3-N (e.g., Coweeta or Walker Branch) do not necessarily exhibit large outputs. Loses through streamflow are small, in relation to the amount of N taken up by the forest. Two variables play a key role in the formation and transport of mineral-N in forest soils: microbial transformations regulate the amount of NO_3-N production, and vegetative uptake can be effective in regulating NO_3-N leaching from the root zone. Some soils readily produce NO_3-N; the tolerant hardwood Turkey Lakes soil is a good example. Other soils exhibit very low rates of nitrification, e g., boreal coniferous forest soils. Hence, NO_3-N discharge in streamwater was much higher at Turkey Lakes than in two boreal conifer water-sheds in northern Ontario (Table 3) The importance of vegetative uptake in controlling streamflow NO_3-N outputs can be demonstrated by comparing NO_3-N discharges in relation to varying degrees of forest removal (Table 4). In New Hampshire forests, NO_3-N discharge increased with the degree of vegetation removal. At Hubbard Brook, Likens et al. (1977) have reported that NO_3-N losses were low during the growing season, but after cessation of vegetative growth and N uptake in the autumn, streamflow discharge of NO_3-N increased markedly. Response to forest removal is less dramatic in watersheds with soils that have low rates of nitrification, e.g., Coweeta. Nitrate-N losses, therefore, are strongly regulated by both microbial transformations and vegetation uptake rather than by levels of atmospheric inputs. Increased NO_3-N discharge generally contributed to increased Ca losses from ecosystems (Table 4). Sulphate discharge, however, is relatively unaffected by vegetation control (Table 4).

Table 3. Annual precipitation input and streamflow output of nutrients (kg ha^{-1}) in eastern North American forest watersheds

Watershed	Nitrogen[a]		Nitrate-N		Sulphate-S		Total Base Cations[b]		Reference
	Input	Output	Input	Output	Input	Output	Input	Output	
ELA, Ont.	6.96	2.76	1.73	0.12	4.13	10.23	6.91	19.16	Nicolson et al. 1982, Schindler (pers. commun.)
Orient Bay, Ont.	5.44	2.38	1.68	0.21	8.53	6.39	15.70	47.64	Nicolson (unpubl.)
Turkey Lakes, Ont.	11.75	7.06	6.10	5.24	10.21	11.89	10.40	36.41	Nicolson 1984
Hubbard Brook, N.H.	20.7	4.0	4.45	3.86	12.82	17.96	5.23	25.95	Likens et al. 1977
Coweeta, N.C.	6.39[c]	0.16[c]	3.65	0.10	13.75	3.36	14.58	31.94	Swank and Douglas 1977
Walker Branch, Tenn.	13.0	3.1	3.9	0.2	18.1	11.5	23.4	235.8	Henderson and Harris 1975 Henderson et al. 1977

[a] NH_4-N + NO_3-N + organic-N.

[b] K, Ca, Mg, Na.

[c] NH_4-N + NO_3-N.

Table 4. Additional element loss (kg ha^{-1} yr^{-1}) in streamflow after forest disturbance

Disturbance	Time (years)	Nitrate-N	Sulphate-S	Calcium	Reference
Strip cutting, N.H.	2	6.0	-0.8	4.9	Hornbeck et al. 1975
Clearcutting, N.H.	2	47.5	–	44.5	Likens et al. 1978
Devegetation, N.H.	2	123.5	-3.0	73.8	Likens et al. 1970
Clearcutting, N.B.	3	6.3[a]	–	–	Krause 1982
Clearcutting, West Va.	3	1.3	-0.3	1.1	Aubertin and Patric 1974
Fertilization, West Va. (258 kg N ha^{-1})	1	45.1	–	–	Aubertin et al. 1973

[a] NH_4-N + NO_3-N + organic-N.

SULPHUR CYCLE

Sulphate, like NO_3, is being deposited in significant quantities on eastern forests by acid precipitation. According to the anion mobility concept advanced by Cole and Gessel (1965), mobile anions provide counterions for cation transfer through the soil. Increased SO_4 concentrations in soil solution result in increased transport of cations (bases, H and Al). In eastern North American forest floors, SO_4 contributes an equivalent of no less than 25% and as much as 64% of the charge balance for base cations in percolate (Table 5). Organic acids and NO_3 also contribute significantly to balance cations. At Mount Moosilauke, New Hampshire, and Solling, West Germany, much of the SO_4 is derived from canopy wash. Leaching of K, Ca. and Mg from forest canopies is a significant source of cations for the forest floor percolating waters (Eaton et al. 1973; Mollitor and Raynal 1982; Foster and Nicolson 1983).

An examination of SO_4 levels in coniferous forest floors from western North America, where throughfall SO_4 concentrations are lower than in the east, reveals that between 10 and 35% of base cation movement is associated with SO_4 (Table 6). Organic acids and/or bicarbonate (HCO_3) ions are the major anions in the percolates.

In western forests soil percolate collected below the rooting zone contains SO_4 concentrations of 20 to 50 µeq L^{-1}, equivalent to 10 to 20% of total base cation concentrations (Table 6). In western forests HCO_3 ions provide the negative charge balance for base cations, but in the more acid eastern soils HCO_3 concentrations are low. In eastern forests the quantity of cations transported with SO_4 increases as water percolates from the forest floor, through the mineral soil, to the lower limit of tree rooting. Sulphate concentrations (ca. 130 to 240 µeq L^{-1}) are equal to 70 to 80% of the total base cation concentration, on an equivalent-weight basis, in water below the rooting zone (Table 5). Water moving below the rooting zone has higher SO_4 concentrations but lower concentrations of total base cations than that entering the soil from the forest floor. Cations transported by NO_3 and organic acids from the forest floor during the growing season are deposited largely in the upper mineral soil horizons or are taken up by the forest. Cation leaching from the rooting zone with NO_3 increases during the dormant period. A selectivity for divalent cation exchange (Ca, Mg) would also be expected in mineral horizons. Because of the major role of SO_4 in cation movement from the rooting zone of eastern forests, the total cation concentrations are as great as those observed in western forests. A reduction in the quantity of SO_4 entering eastern forest soils would likely result in moderated cation losses from these ecosystems.

Simulation models that calculate cation and anion loss from soils as a function of soil and rainfall characteristics have been developed. Reuss (1980) has developed a model in which sorption and chemical equilibria reactions mathematically describe the distribution of ions between the solution and solid phase in soil. The model predicted an equivalence between strong acid input and cation export from the soil if the lime potential of the soil is greater than three. Reuss (1980) states: "As the lime potential and base saturation of the soil decreases, acid precipitation causes leaching of hydrogen and Al ions, instead of bases. Soils well supplied with bases are most susceptible to base loss".

In very strongly acid soils in the eastern forests the cation exchange capacity is dominated by H and/or Al. Mobile SO_4 ions may enhance Al leaching from the large exchangeable pool of Al in the soil (e.g., Cronan 1980). When dilute sulphuric acid is applied to very strongly acid podzolic soils in a simulated leaching experiment, SO_4 first removes base cations from the soil (Morrison 1983). When loadings of acid are continued, base cation leaching declines and Mn and Al are transported with SO_4. In acid soils with low base saturation, such as the Becket soil at Hubbard Brook, New Hampshire, and Huntington Forest, New York, Al and Mn dissolution and transport are likely. Mollitor and Raynal (1982) reported average Al concentrations of 182 and 307 $\mu eq\ L^{-1}$ for hardwood and conifer mineral soil leachate at Huntington Forest. Aluminum ions made a significant contribution to total cation concentrations in percolate. Increases in Al concentrations in soil solution over a 13-year period in a beech (*Fagus silvatica* L.) soil at Solling, West Germany, have been documented by Ulrich et al. (1980). High concentrations of SO_4 in percolate from the Dystric-Brunisolic (Typic dystrochrept) soil in beech and Norway spruce (*Picea abies* (L.) Karst.) forest at Solling (Ulrich, pers. Commun.) were associated with Al concentrations of 200 to 1800 $\mu eq\ L^{-1}$, and higher total cation concentrations than those observed in North American soils.

OUTPUT

Total base cation concentrations in waters leaving the rooting zone of the eastern watersheds are, on average, 10 times greater than the concentrations in incident precipitation. In the absence of data on volume flow, however, it is not possible to calculate accurately the flux of elements from the rooting zone. Elements leaching from the rooting zone contribute to streamflow outputs from the ecosystem. Streamflow, however, includes elements leached from unsaturated and saturated soil below the rooting zone and bedrock in contact with groundwater.

When significant SO_4 adsorption occurs in soil, the loss of base cations, H, and Al ions will occur at a rate slower than that predicted from acid inputs. The importance of SO_4 adsorption in soil is revealed when inputs and outputs of SO_4-S in eastern watersheds are examined (Table 3). Sulphur is accumulating in hardwood forests at Coweeta, North Carolina, and Walker Branch, Tennessee. Johnson et al. (1980) have determined that highly weathered hapudult and paleudult soils in these watersheds contain significant amounts of insoluble SO_4- S (20 to 65 ppm) and hapudult soils adsorb additional SO_4-S (15 to 70 ppm).

Conifer and hardwood watersheds with podzol soils generally export as much SO_4-S as they import from the atmosphere. Turkey Lakes soil from the Bhf and Bf horizons contained and adsorbed 0 to 40 ppm of SO_4-S. Johnson et al. (1980) reported that the Hubbard Brook Becket podzol contains no insoluble SO_4-S and adsorbs only small amounts of insoluble SO_4-S (5 to 13 ppm). Some podzolic soils, therefore, appear to have low rates of SO_4 adsorption. We have already pointed out that SO_4 is the dominant anion associated with cation movement out of the rooting zone of eastern podzolic soils.

In the Becket soil at Huntington Forest, most of the total S is in organic combination, largely carbon bonded with smaller amounts of ester sulphate (David et al. 1982). David et al. (1982) have suggested that the quantity of SO_4 mineralized from soil organic reserves is well in excess of that entering the forest floor in throughfall. A large internal S cycle may be active within these and other eastern forest ecosystems. Conclusions concerning the importance of atmospheric SO_4-S on cation leaching, therefore, must be regarded with caution because of incomplete knowledge of S dynamics in eastern forest ecosystems.

Table 5. The concentration of ions (μeq L^{-1}) in water within eastern North American forest ecosystems and Solling forest, West Germany

Forest	Throughfall	Forest floor	Forest floor	Below rooting		Reference
	Sulphate		Total cations[a]	Sulphate	Total cations[a]	
Acer saccharum Marsh. (N.Y.) *Betula alleghaniensis* Britton *Fagus grandifolia* Ehrh.	88	82	327	209	227	Mollitor and Raynal 1982
Acer saccharum Marsh. (Ont.) *Betula alleghaniensis* Britton	96	127	290	170	241	Foster (unpubl.)
Tsuga canadensis (L.) Carr. (N.Y.) *Betula alleghaniensis* Britton *Picea rubens* Sarg.	141	131	476	242	355	Mollitor and Raynal 1982
Abies balsamea (L.) Mill. (N.H.) *Betula papyrifera* var. *cordifolia* (Reg.) Fern. *Picea rubens* Sarg.	143	137	213	132	163	Cronan 1980
Fagus silvatica L. (Solling)	281	436	863	293	591	Heinrichs and Mayer 1977
Picea abies (L.) Karst. (Solling)	655	705	1143	449	730	Heinrichs and Mayer 1977

[a] K, Ca, Mg, Na.

Table 6. The concentration of ions (µeq L^{-1}) in water within western North American forest ecosystems

Forest	Throughfall	Forest floor	Forest floor	Below rooting	
	Sulphate		Total cations[a]	Sulphate	Total cations[a]
Tsuga heterophylla (Raf.) Sarg. (Alaska) *Picea sitchensis* (Bong.) Carr.	23	217	595	22	179
Pseudotsuga menziesii (Wash.) (Mirb.) Franco	24	144	429	43	239
Tsuga heterophylla (Raf.) Sarg. (Alaska) *Picea sitchensis* (Bong.) Carr.	38	51	539	24	344
Abies amabilis (Dougl.) Forb. (Wash.) *Tsuga mertensiana* (Borg.) Carr.	64	51	225	49	298

[a] K, Ca, Mg, Na.

Source: Johnson 1975, 1981.

All watersheds lost more cations than they received from the atmosphere (Table 3). Output:input ratios of between 2:1 and 5:1 are observed in watersheds in soil derived from resistant igneous bedrock or metamorphic equivalents. Outputs exceed inputs by a ratio of 10:1 at Walker Branch, Tennessee, on soil derived in situ from less resistant dolomitic bedrock.

Recent advances have been made in developing simulation models to predict surface water response to changes in atmospheric inputs of elements. In two models, the "ILWAS" model (Integrated Lake-Water Acidification Study-EPRI) described by Chen et al. (1982) and the "BIRKENES" hydrochemical model (Norwegian SNSF-project) of Christophersen and Wright (1981), inputs that drive the models are precipitation quality and quantity and weather parameters. Both models consider physical and chemical reactions within the soil, and "ILWAS" also evaluates reactions within the forest canopy. Because of site specificity in the development and testing of these models, considerable model modification may be necessary if a universal model, transferable to other watersheds, is possible.

CONCLUSIONS

Acid precipitation, in the short term, increases the addition of mobile anions (SO_4, NO_3) to eastern North American forests. These anions enhance the leaching of base cations from the forest canopy and forest floor. At current levels, inputs of SO_4-S contribute significantly to cation losses from the rooting zone, including bases, H, and Al in many eastern ecosystems. Nitrate-N additions, being largely retained within the ecosystem, augment soil supplies of mineral N. Meteoric N is more likely to benefit the productivity of conifer forests, in which N is often limited, than that of hardwoods.

It is not yet possible to determine whether acid precipitation will induce long-term changes in nutrient cycling that will influence forest productivity. For example, short-term increases in nutrient cycling may be counteracted by decreased decomposition, which will increase the residence time of nutrients in the forest floor. Many forest soils in the region are already highly acid, with considerable acidity produced by natural processes within the ecosystem. In our view, SO_4 inputs from acid precipitation are likely to produce the most serious long-term changes in nutrient cycling, because of the low SO_4 adsorption character of some eastern podzolic soils. Rates of mineral weathering in these soils may not be fast enough to replace bases leached from foliage and exchange sites in the soil. Solubilization of Al and/or Mn will increase the concentration of these elements in the soil solution.

Forest scientists must improve their ability to make reliable forecasts based on their understanding of natural processes affecting nutrient cycling. Recent applications of simulation techniques to modelling of nutrient cycles may help us predict the extent of the effects of long-term acid rain on nutrient cycles.

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Chemical Characteristics of Precipitation, Stream Flow, Lake Water and Sediments Quality in Northern Temperate Forest Watersheds Threatened by Acidic Atmospheric Inputs

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ABSTRACT

Studies were carried out on the spatial and temporal distribution of certain chemical parameters of precipitation, lake water quality and paleolimnological profiles of the sediments in certain forested watersheds in the Laurentides Park, Québec. The results establish the current response of watersheds to the present acidic atmospheric loading and indicate recent perturbations in the natural chemical flux within these systems.

The effect of forest cover on the chemical characteristics of individual rain events in the spring and summer seasons is greater in magnitude than the variability between incoming precipitation episodes. On the other hand, stream flow quality is little affected by changes in throughfall and seems to be more associated with total anion charge rather than pH levels *per se*. The winter accumulation of acidic pollutants in the snow pack leads to an appreciable depression of pH levels during snowmelt with concomitant increases in aluminum concentrations and manganese/iron ratios of the stream waters.

The subsequent reaction of lacustrine waters to the chemical nature of their tributaries is reflected over a number of years by a progressive increase in the clarity of the lakes, lower mean annual pH values and lowered photosynthetic production in the pelagic zone.

Long-term changes in the water quality of the tributaries are reflected in the chemical profiles of such metals as Al and Mn in the most recent (0-100 years) lake sediments, although the precise nature of the concentration patterns is dependent on thermal stratification, hypolimnetic pH values and anoxic conditions at the sediment-water interface. Lake sediments may also reflect past direct deposition patterns on the lake surface. The Pb, Zn and Hg concentration profiles in the upper 0-30 cm layer are good indicators of pollutant-load fluctuations in the recent past. A more complex type of profile is shown by ^{137}Cs, which shows different patterns of concentrations in the surficial 0- to 10-cm layer of lake sediments. This is dependent on the nature of the watershed vegetation. In forested watersheds, the lake stratigraphic distribution curve of ^{137}Cs suggests that the presence of significant ground and herbaceous layers acts as a sink for the isotope; this contrasts with the lake sediment profiles in agricultural watersheds where the ^{137}Cs distribution is more closely correlated with its known contemporary atmospheric production.

INTRODUCTION

The pathways of acidic pollutants among atmospheric, terrestrial and aquatic systems in relation to the acidification of precipitation and surface waters are currently receiving a great deal of attention (Likens and Bormann 1974a; Hasler 1975; Galloway et al. 1980a, 1980b; Goldstein et al. 1980; Gorham and McFee 1980; Herrmann and Baron 1980; Horntvedt et al. 1980; Jones and Bisson 1980; Nicholson et al. 1980; Stuanes 1980; Wright and Johannessen 1980; Jones et al. 1983). The perturbation of biogeochemical cycles by the long-range transport of atmospheric pollutants is the result of the effects of direct and indirect deposition of acidic aerosols and of other pollutants (heavy metals, PAH) within catchment areas as well as on the surface of streams and lakes. Because lakes act as the receptors for whole watersheds, the effects of atmospheric pollutants are often amplified within the lacustrine environment, and signs of perturbation of natural cycles have commonly been observed earlier there than in terrestrial systems (Webster 1961; Beamish and Harvey 1972; Likens and Bormann 1974b; Ouellet and Poulin 1975; Dickson 1975; Wright and Gjessing 1976). Cowling (1980), Evans et al. (1981) and Nilssen (1982) have recently summarized the various lake processes which characterize the acidification of surface water.

Spatial and temporal distribution of certain chemical parameters in precipitation patterns, throughfall, stream flow, lake water quality and lacustrine sediments are additional indicators of perturbed biogeochemical cycles in forested watersheds receiving acid precipitation. The objective of the present paper is to discuss the close relationship existing between a lake and its watershed as a function of the atmospheric pollutant loading. The region chosen is within the Québec Laurentides Park which, because of its high precipitation (160 cm), geology and topography, is one of the most acid-sensitive areas of Canada but still relatively poorly studied.

The following paper starts by a broad geographical overview of the pertinent chemical characteristics of wet precipitation over the entire Province of Québec. This is followed by a discussion of the physico chemical characteristics of lakes within the Laurentides Park. Finally, attention is concentrated on a calibrated watershed, Tantaré, where impacts of acid rain on both the terrestrial and aquatic systems have been studied by the authors for the last three years.

MATERIAL AND METHODS

Regional Precipitation Characteristics

Average values for chemical species obtained from the 1981 precipitation chemistry data provided by the Canadian Network for Sampling Precipitation (CANSAP) (Environment Canada 1981; Barrie and Sirois 1982) and from data obtained by the Province of Québec's sampling network (PQPN; Talbot 1981, 1982) have been used to illustrate the geographical patterns for the wet deposition of certain acidic aerosols over the entire Province of Québec. In the tracing of the isopleths (Figs. 1-4), chemical characteristics of the precipitation of stations located outside the province (Moosonee, Kapuskasing, Kingston, Acadia Fes, Charlo, Saint-John, Truro) were also taken into account. Monthly average values obtained from the Canadian Air and Precipitation Monitoring Network (CAPN) at the Montmorency Forest station for the year 1981 (Table 1) (Barrie et al. 1982) have been used to illustrate annual variations in the influx of pollutants in the precipitation over the Laurentide Park. The annual mean values for the chemical composition of precipitation obtained from CAPN at the Montmorency Forest are compared to similar data obtained at the CANSAP station located at the Québec Airport, as well as to the sampling stations of PQPN located at the Montmorency Forest and Mont-Apica (Table 2).

Regional Limnology

In order to establish a relationship between wet precipitation chemistry and the regional chemical characteristics of lakes located within the Laurentides Park, we have used various limnological data (Bobée et al. 1982; Richard 1982; Ouellet and Jones 1983; Ouellet et al., unpublished). The Park (Fig. 5) (located between latitudes 47° and between 48° and longitudes 71° and 72°) is situated entirely within the Laurentide Highlands of the Grenville physiographic province of the Canadian Precambrian Shield. The Park covers an area of about 10^6 hectares and comprises more than 2500 lakes which are ice-free for five to six months of the year. The elevation of the plateau topography, the geology of which is typical of the Shield, varies from 350 to 1148 m; the vegetation of the area has been described by Rowe (1959). The black spruce forest at the higher elevations and the balsam fir, paper birch, white spruce and poplar phytosociological associations on the periphery of the plateau are important sources of timber and cellulose. The surface water of this region is extremely

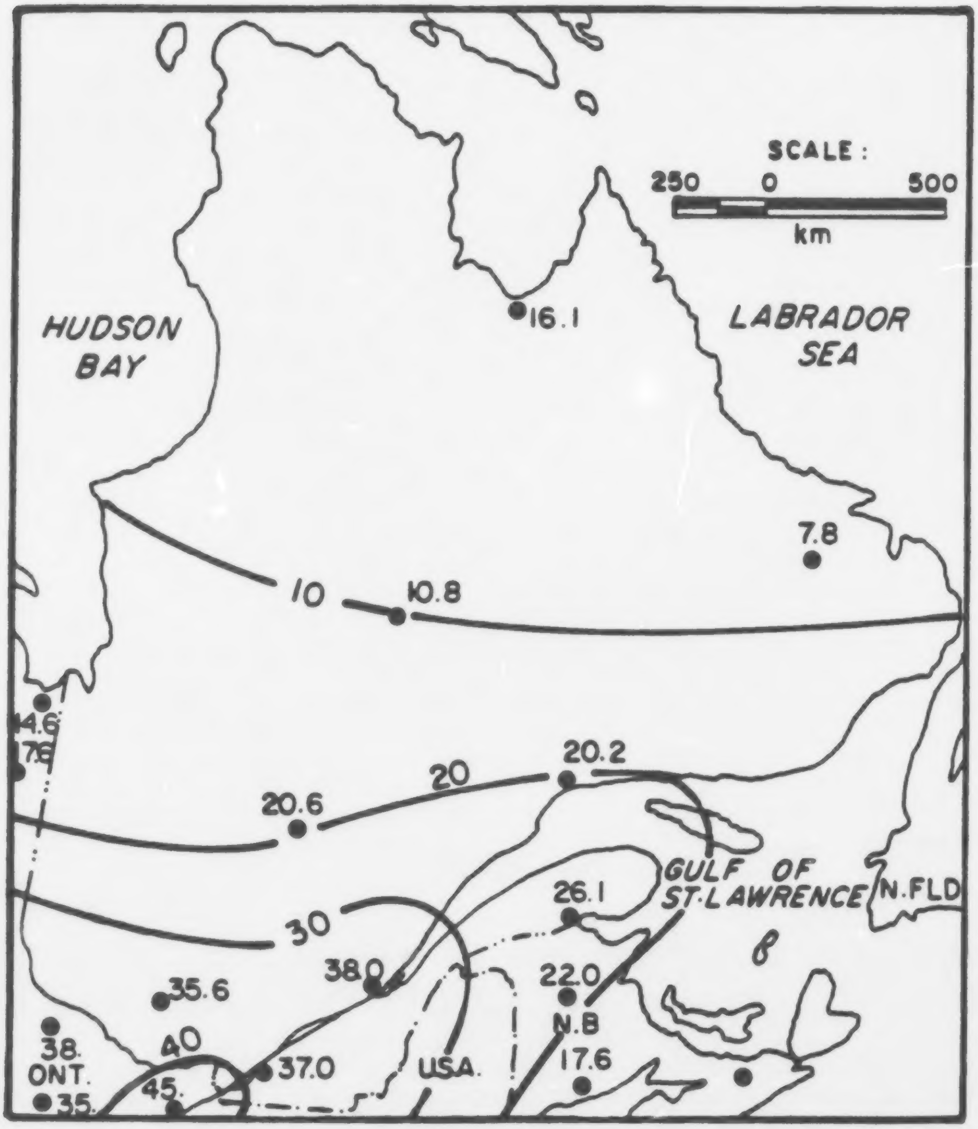
SCALE :
250
0
500
km
HUDSON BAY
LABRADOR SEA
16.1
7.8
10
10.8
4.6
17.6
20.2
20
20.6
GULF OF ST.LAWRENCE
N.FLD
26.1
30
38.0
35.6
22.0
N.B
38.
ONT.
40
37.0
USA.
17.6
45.
35.

Figure 1. Spatial distribution over the Province of Québec of the annual mean precipitation conductivity (μmho cm^{-1}) for the year 1981 (adapted from CANSAP data).

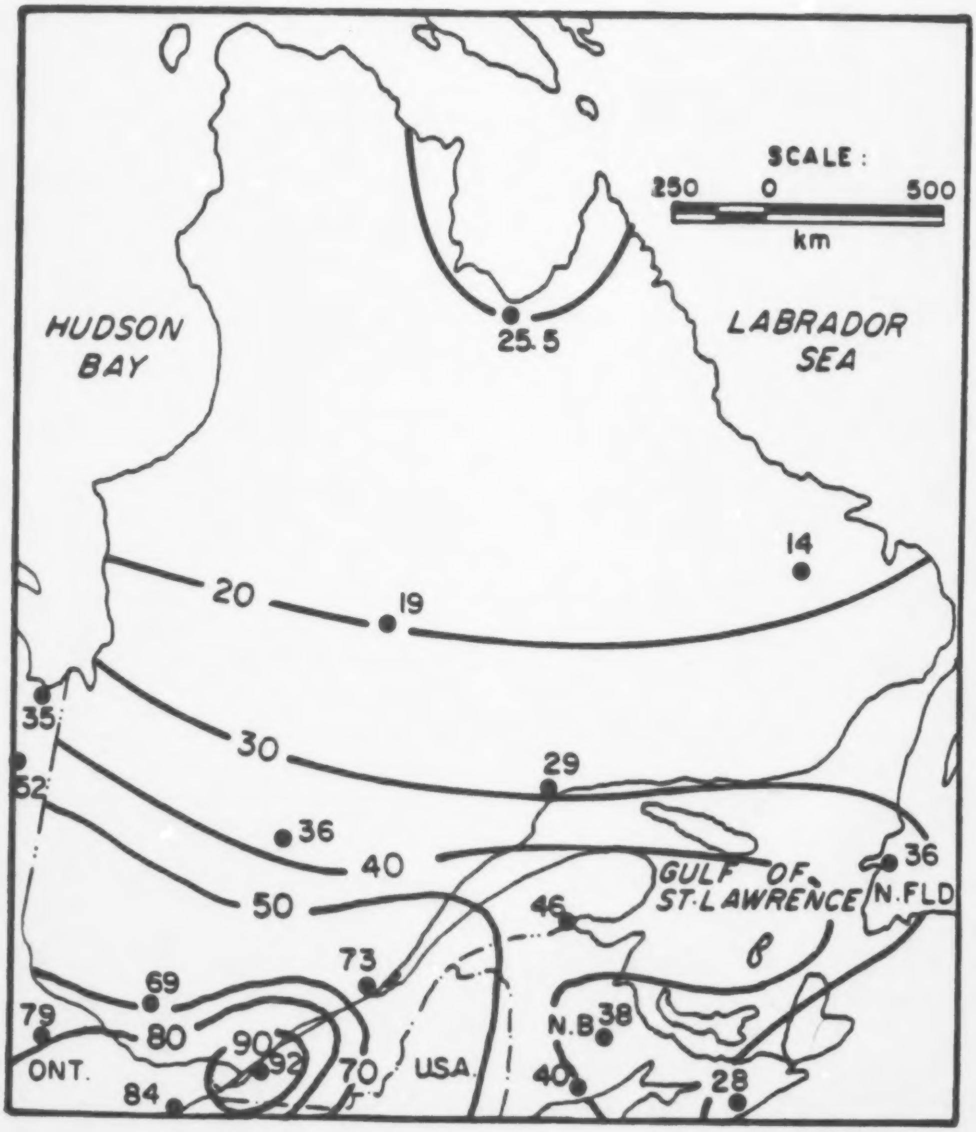
SCALE :
250
0
500
km
HUDSON BAY
LABRADOR SEA
25.5
14
20
19
35
30
29
52
36
40
36
50
GULF OF ST. LAWRENCE
N.FLD
46
73
69
N.B
38
79
80
90
92
70
USA.
40
28
ONT.
84

Figure 2. Spatial distribution over the Province of Québec of the annual mean precipitation SO_4^{2-} concentration (µeq L^{-1}) for the year 1981 (adapted from CANSAP data).

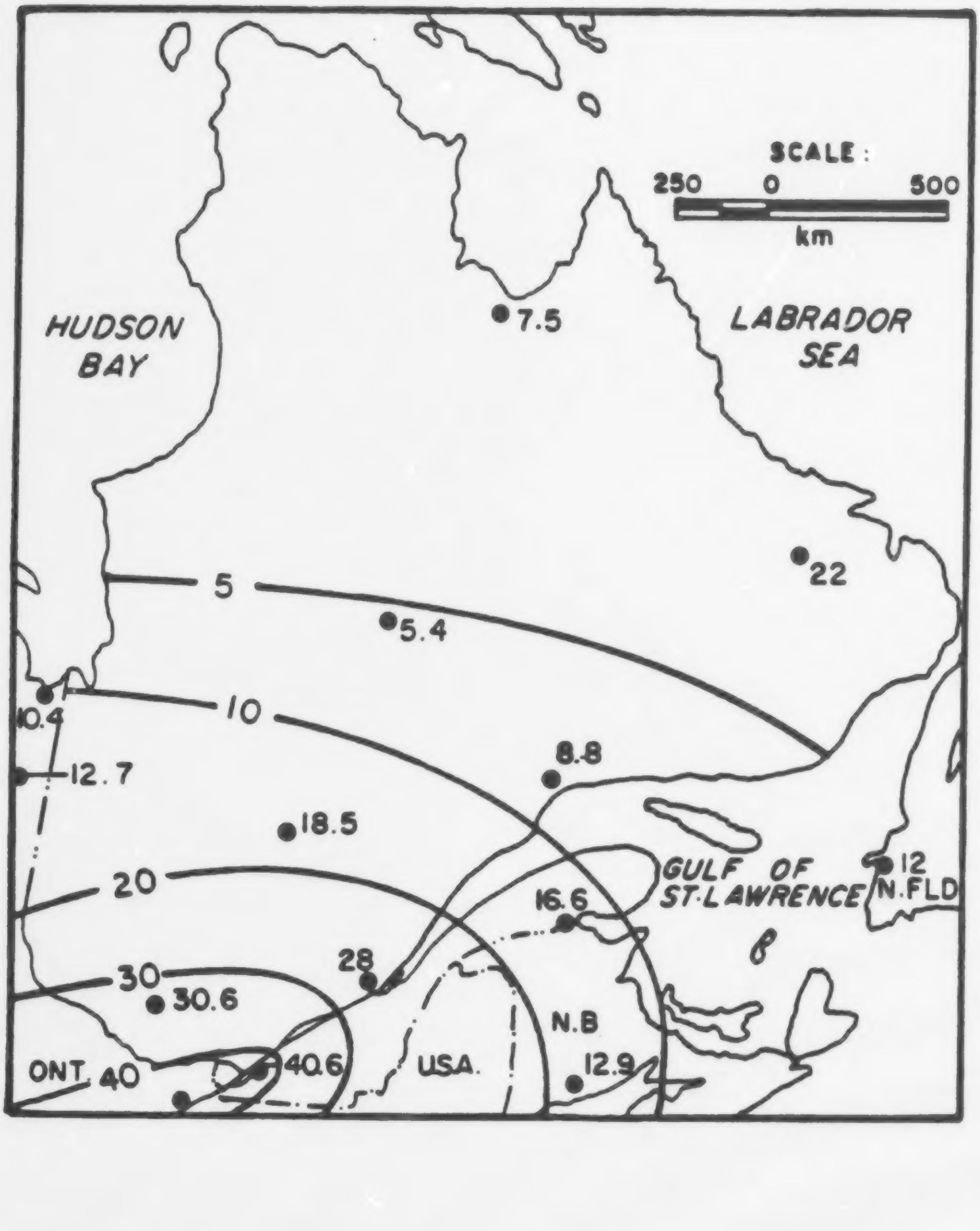
SCALE:
250
0
500
km
HUDSON BAY
LABRADOR SEA
GULF OF ST·LAWRENCE
N.FLD
N.B
USA.
ONT.
7.5
22
5
5.4
10
10.4
12.7
8.8
18.5
20
12
16.6
28
30
30.6
40
40.6
12.9

Figure 3. Spatial distribution over the Province of Québec of the annual mean precipitation NO_3^- concentration (μeq L^{-1}) for the year 1981 (adapted from CANSAP data).

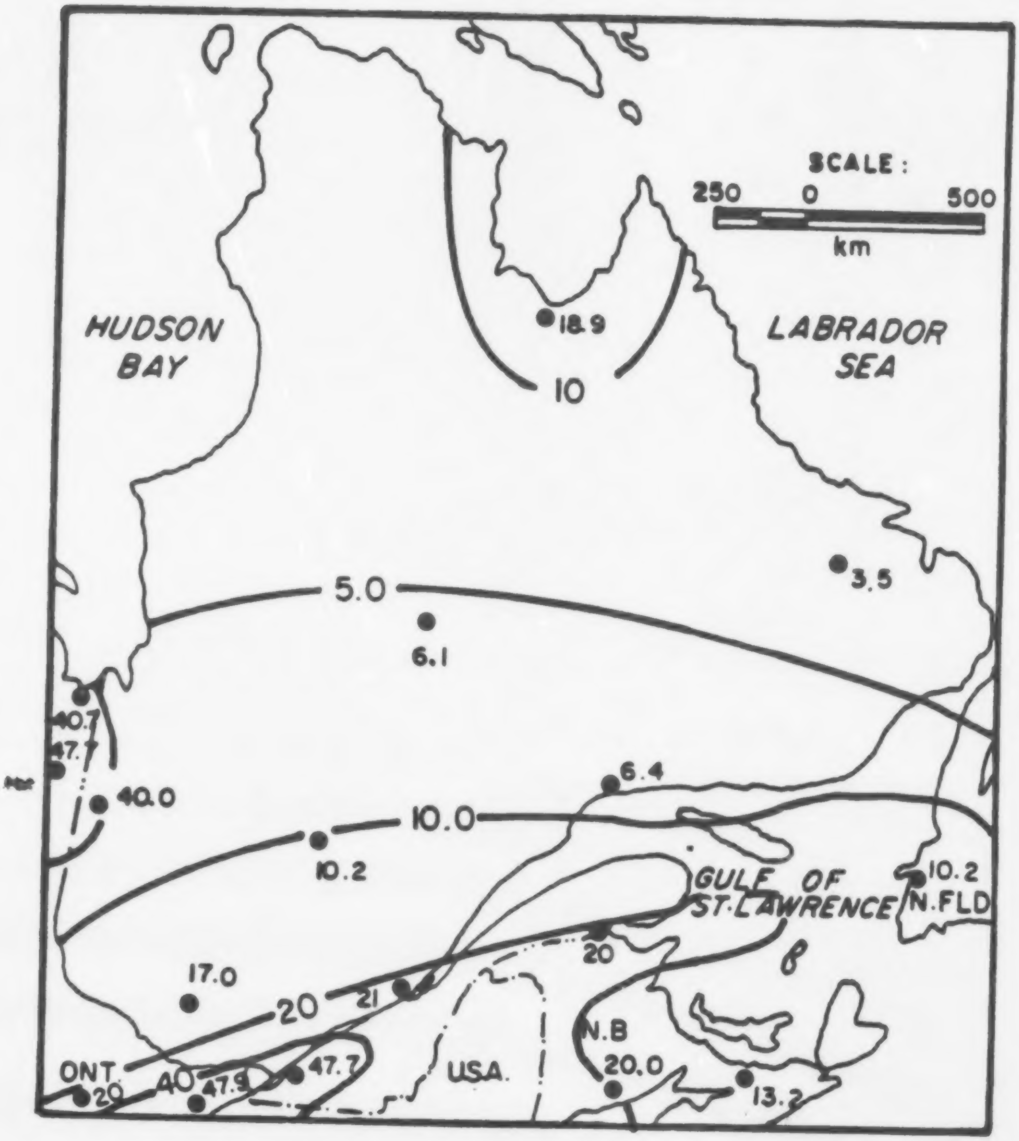
SCALE :
250
0
500
km
HUDSON BAY
LABRADOR SEA
18.9
10
5.0
6.1
3.5
40.7
47.7
40.0
6.4
10.0
10.2
GULF OF ST·LAWRENCE
10.2
N.FLD
20
17.0
20
21
8
N.B
ONT.
20
40
47.9
47.7
USA.
20.0
13.2

Figure 4. Spatial distribution over the Province of Québec of the annual mean precipitation Ca^{2+} concentration (μeq L^{-1}) for the year 1981 (adapted from CANSAP data).

Table 1. Mean monthly precipitation chemistry for the year 1981 at the Montmorency Forest monitoring station of the Canadian Air and Precipitation Network (data compiled from Barrie et al. 1982)

	1981												
Parameter	J	F	M	A	M	J	J	A	S	O	N	D	X
H^+ µeq L^{-1}	19.95	20.42	13.18	25.70	54.95	29.51	32.36	32.36	26.92	25.12	43.65	3.09	27.26
	6*	10	10	11	13	9	8	12	14	20	11	17	141
SO_4^{2-} µeq L^{-1}	28.60	30.60	26.50	42.90	75.60	55.20	49.00	36.80	40.90	36.80	38.80	22.50	40.35
	7	14	13	12	14	12	10	13	15	20	13	18	161
NO_x^- µeq L^{-1}	42.70	37.80	16.90	36.60	26.50	11.80	13.04	9.66	7.32	17.20	12.40	7.11	19.90
	7	13	10	10	12	9	7	13	11	16	5	5	118
Cl^- µeq L^{-1}	11.80	17.50	8.00	1.40	1.40	< 1.40	3.00	< 1.40	5.70	2.80	4.50	21.40	6.69
	7	14	13	12	14	12	9	13	15	20	13	19	161
Ca^{2+} µeq L^{-1}	8.50	4.20	3.80	20.00	13.00	4.50	5.55	3.50	3.00	5.50	9.00	10.00	7.54
	4	10	8	12	14	9	5	13	7	16	8	10	116
NH_4^+ µeq L^{-1}	5.80	7.70	7.80	22.40	21.40	12.40	11.00	7.70	14.80	7.20	0.70	1.30	10.02
	7	14	10	10	12	9	7	13	11	16	5	5	119
Mg^{2+} µeq L^{-1}	1.64	1.11	0.49	4.09	3.27	0.82	0.65	0.24	0.34	0.86	2.66	2.95	1.59
	4	10	8	12	14	9	5	13	7	16	8	10	116
Na^+ µeq L^{-1}	4.34	9.00	7.60	10.00	8.69	12.50	3.73	3.04	1.98	1.86	6.95	18.60	6.09
	4	10	8	11	13	9	5	13	7	16	8	11	115
K^+ µeq L^{-1}	0.69	0.20	0.38	0.76	0.80	0.39	0.10	0.11	0.18	0.11	0.89	2.49	0.59
	4	10	8	11	13	9	5	13	7	16	8	11	115
Σ cations µeq L^{-1}	40.92	42.63	33.25	87.95	102.11	48.87	53.34	46.95	47.22	40.65	63.85	38.43	53.09
Σ anions µeq L^{-1}	83.10	85.90	51.40	80.90	103.50	68.40	65.04	47.86	53.92	56.80	55.70	51.01	66.94
t°C	-18.3	-7.4	-6.6	0.3	7.2	12.1	15.0	13.8	8.6	2.0	-3.0	-8.7	1.25
ppt (mm)	54.90	247.40	156.80	137.50	133.30	194.80	78.20	180.20	105.90	117.20	60.60	99.60	130.57

*number of observations

Table 2. Mean annual precipitation chemistry for the Québec City area and the Laurentides Park

VARIABLE	CANSAP[1] Québec	CANSAP[2] Québec	CAPN[3] Montmorency	PQPN[4] Montmorency	PQPN[5] Apica
H^+ µeq L^{-1}	33.01	63.00	27.26	47.49	41.74
SO_4^{2-} µeq L^{-1}	105.90	73.21	40.35	41.10	49.59
NO_x^- µeq L^{-1}	37.10	28.51	19.90	26.76	20.20
Cl^- µeq L^{-1}	16.10	10.46	6.69	4.17	10.44*
Ca^{2+} µeq L^{-1}	51.03	21.06	7.54	4.76	8.85
NH_4^+ µeq L^{-1}	32.21	23.10	10.01	15.18	11.54
Mg^{2+} µeq L^{-1}	4.75	2.87	1.59	1.45	1.46
Na^+ µeq L^{-1}	10.89	5.37	6.01	2.51	13.81*
K^+ µeq L^{-1}	3.27	1.37	0.5[illegible]	0.62	0.92
HCO_3^- µeq L^{-1}	—	—	—	0.22	0.0
Σ cations µeq L^{-1}	151.25	116.77	53.09	72.13	78.32
Σ anions µeq L^{-1}	159.91	112.18	66.94	72.03	80.23
Conductivity (µmho cm^{-1})	42.84	38.80	—	14.00	

[1] Québec Airport, CANSAP-Data, 1977-1981 (n = 41-44)
[2] Québec Airport, CANSAP-Data, 1981 (n = 8)
[3] Montmorency Forest, CAPN-Data, 1981 (n = 115-141)
[4] Montmorency Forest, PQPN-Data, 1982 (n = 348)
[5] Mont Apica, PQPN-Data, 1982 (n = 178)

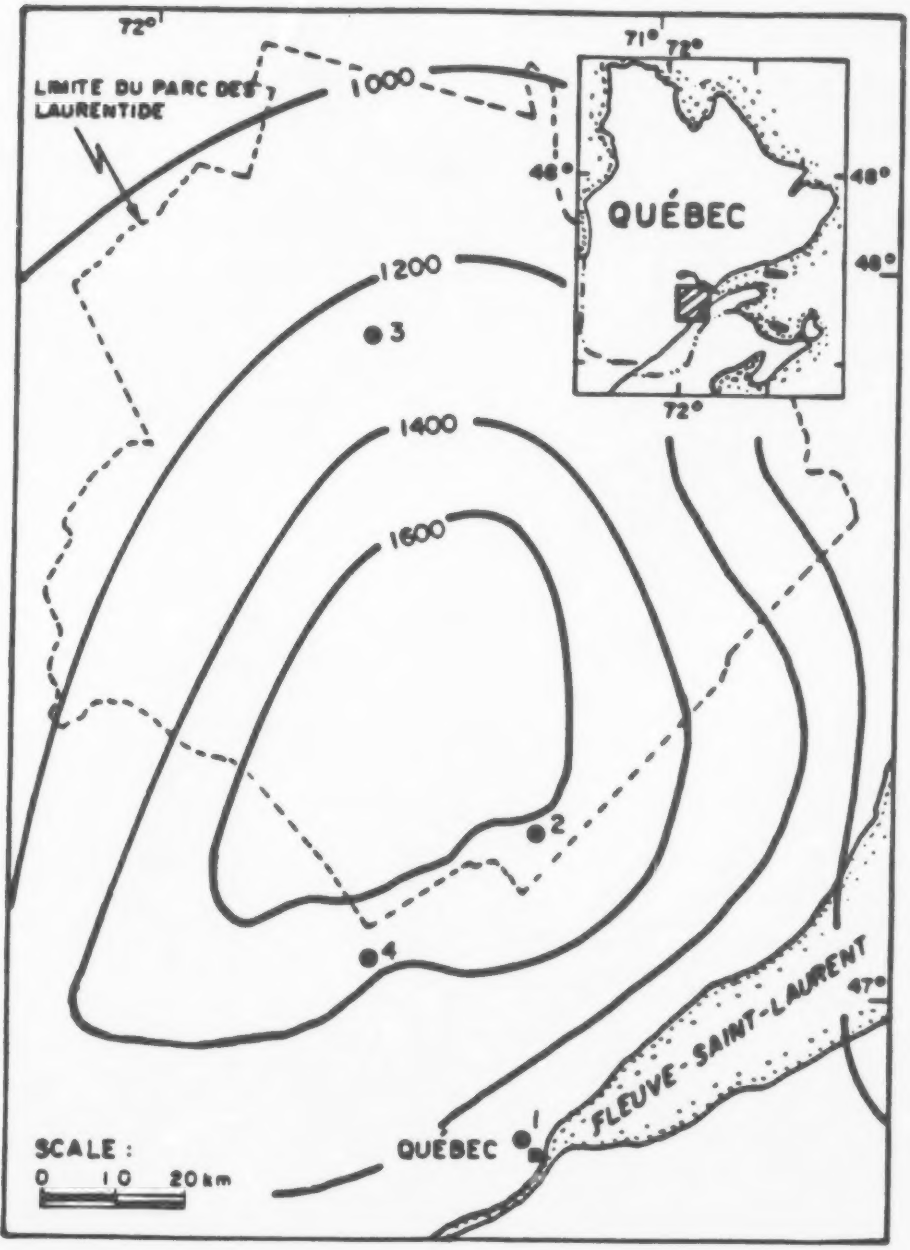
72°
LIMITE DU PARC DES LAURENTIDE
1000
71°
72°
48°
QUÉBEC
48°
46°
1200
3
72°
1400
1600
2
4
FLEUVE SAINT-LAURENT
47°
1
QUÉBEC
SCALE :
0 10 20 km

Figure 5. Total mean annual precipitation (mm) over the Laurentides Park area and location of studied sites (1- Québec Airport CANSAP station; 2- Montmorency CAPN and PQPN stations; 3- Mont-Apica PQPN station; 4- Lake Tantaré).

Table 3. Average chemical composition of the precipitation, throughfall, stream and lakes for the Laurentides Park area

Variable	1	2	3	4	5
H^+ µeq L^{-1}	38.83	1.12	25	7.94	1.20
SO_4^{2-} µeq L^{-1}	43.68	51	92	118.70	84.80
NO_x^- µeq L^{-1}	22.68	13	6	8.54	2.09
Cl^- µeq L^{-1}	8.76	4.3	9	8.57	11.40
Ca^{2+} µeq L^{-1}	7.05	15	50	75.00	125.00
NH_4^+ µeq L^{-1}	12.24	--	--	--	--
Mg^{2+} µeq L^{-1}	1.50	25	17	15.38	43.30
Na^+ µeq L^{-1}	8.77	8	26	21.73	41.30
K^+ µeq L^{-1}	0.71	33	9	7.69	4.70
Alkalinity mg $CaCO_3$ L^{-1}	--	--	--	--	188.33
Al µg L^{-1}	--	10	350	22.00	110.00
Fe µg L^{-1}	--	50	100	40.00	111.50
Mn µg L^{-1}	--	400	20	40.00	21.00
Σ cations µeq L^{-1}	69.10	82.12	127.0	127.74	215.50
Σ anions µeq L^{-1}	75.12	68.3	107.0	135.81	286.62
Conductivity	14.00	31.2	26.4	18.00	24.00
N	641-667	4	8		104

1 : Precipitation average from the CAPN and PQPN
2 : Tantaré watershed, yellow birch throughfall (1982)
3 : Lake Tantaré, stream B
4 : Lake Tantaré (Ouellet and Jones 1983)
5 : Lake Laflamme (Papineau 1983)

soft (Table 3), and conductivity values above 50 µmho cm^{-1} are rare, (mean of 22.5) if lakes affected by runoff containing road salt in areas close to the main highway are excluded. The concentration of minerals in the surface water in the extreme northwest part of the Park (Belle Rivière area) is somewhat higher, and the surface water has a pH often slightly above 7. This is due to the weathering of surficial calcareous sediments, which were transported by glaciers and originated from the Trenton paleozoic limestone formation located on the south bank of Lake St. John, approximately 30 km north of the Park. Surficial waters with pH values below 5.5 are common within the rest of the Park.

The total annual precipitation of the region (maximum 160 cm; 30% as snow) is one of the highest for eastern Canada, and its geographical distribution is strongly influenced by the region's topography. Although lumbering is an occasional activity of importance within the limits of the Park, the area does not support any permanent settlement. Sport fishing of brook trout (*Salvelinus fontinalis*) has been an important activity for several decades (Richard 1982).

Experimental Watershed

The Tantaré experimental watershed, within the Tantaré ecological reserve, is located at the southern tip of the Laurentides Park (Fig. 5) and is part of the catchment area of the Jacques Cartier River which drains into the St. Lawrence River via the southwestern face of the Laurentide Highlands. Its watershed (41°04'N, 71°33'W; 500 m asl; surface area 12.1 km^2) consists of a mixed-forest cover of the St. Lawrence Lowlands type (maple, yellow birch) associated with boreal stands (fir, spruces, white birch) especially at higher elevations (Desloges and Lachance 1977). The lake comprises four different basins totalling an area of 1.33 km^2 with a maximum water depth of 22 m (Fig. 6). The first (eastern basin) has a shallow mean depth of about 2.5 m, is not thermally stratified in summer and is joined by a narrow shallow (~1 m) water passage to the three others. The watershed does not support any permanent human activity. An investigation of diatoms preserved in the sediments of the eastern basin (Dickman et al. 1981) suggests a recent decrease in pH of the water column. The present pH values of the main water body vary from 4.9 to 5.2 and have favored the development of a small discontinuous algal mat (*Mougeotia*); the hydro-macrophyte community is dominated by *Isoetes*, apparently since the early 1950s (H. Ross, Ecotan ltée, Québec City, personal communication, 1980). The pH levels (Table 3) of the lake reflect the low pH values of the intermittent tributaries (Fig. 6). The streams, which run largely directly on crystalline bedrock, are very poorly buffered, with pH values of 4.2-4.7. The main basin of the lake is well stratified in late summer, and the epilimnetic chemical composition and pH at that time reflect those of the streams. Secchi disc transparency measurements show an unusual depth of 11 m in late summer. The growth of brook trout (*Salvelinus fontinalis*), the only fish population present, is seriously perturbed by the acid stress (Frenette 1984).

Incident precipitation, throughfall and stream waters were sequentially sampled during individual events at stations located on the east shore of the first basin during the 1982 summer season. The stream B (northeast corner of the first basin) and the lake were simultaneously sampled and studied during the major part of 1982. Comparative chemical data for the incident precipitation and throughfall, as well as for the stream and lake, are reproduced in Table 3. Analytical methods for the various chemical parameters are described by Jones and Bisson (1980) and MEQ (1982).

The geochemical characteristics of the surficial sediments of the eastern basin were determined by a study of samples from 35 sites well distributed over the whole basin. In addition, cores were taken at the deepest points of the first and second basins (Fig. 6). Sampling techniques and analytical methods of the lacustrine sediments are described in Ouellet (1980, 1981) and in Guimont and Pichette (1979).

RESULTS AND DISCUSSION

Regional Precipitation Characteristics

Geographical aspects

Transport and deposition patterns in the eastern half of the North American continent have been derived largely from SO_4^{2-} and NO_3^- data collected by the CANSAP and MAP3S precipitation networks (MAP3S/RAIN Research Community 1982; Wilson et al. 1982; Wisniewski and Keitz 1983). It should be noted that these networks comprise relatively few sampling stations distributed over a very large territory. Based on the 1981 CANSAP data, Figures 1 to 4 show that conductivity (Fig. 1), SO_4^{2-} (Fig. 2), NO_3^- (Fig. 3) and Ca^{2+} (Fig. 4) of wet precipitation exhibits, over the entire province, a spatial distribution in which concentrations tend to increase towards the southwest. Within the more densely populated area of the St. Lawrence Lowlands (Kingston - Montréal - Québec), these concentration gradients, especially for NO_3^- and Ca^{2+}, are apparently also influenced by the topography and human activity of the St. Lawrence River Valley. A similar anthropogenic pollutant gradient has been recently described for Pb in lacustrine sediments by Ouellet and Jones (1983).

In order to determine more accurately the origins and impacts of atmospheric pollutants within the Province of Québec the Water Quality Branch of the Québec Ministry of the Environment established a precipitation network of 46 stations restricted to the area south of latitude 56° (Talbot 1981). Preliminary results (PQPN; Talbot 1982) from 29 of the 46 stations, mostly situated within the densely populated part of the province, tend to show a geographical gradient roughly similar to the patterns based on the CANSAP data but much more narrowly restricted along the Kingston - Montréal - Québec axis (Figs. 7 and 8). Because of the great distances (200-300 km) between CANSAP stations, the spatial distribution of SO_4^{2-} and NO_3^- reflects wide inter-state patterns which poorly represent distribution patterns due to regional ($\approx$100 km) characteristics such as topography and urban area. The comparison of these patterns for the same acidic pollutants based on CANSAP and on the Province of Québec data gives an insight into the long-range and regional origins of atmospheric pollutants. For example, the isopleth patterns traced from the provincial network data (Figs. 7 and 8) tend to demonstrate, as do the CANSAP data maps, the existence of long-range atmospheric transport of pollutants originating from the southwest. However, they also indicate the importance of regional sources within the province. In particular, the SO_4^{2-} isopleth pattern traced from the PQPN data shows that the 70 μeq L^{-1} isopleth is strongly restricted to the St. Lawrence Lowlands between Montréal and Québec. This is also shown, but to a lesser extent, by the 30 μeq L^{-1} NO_3^- isopleth. These isopleths reflect the strong regional anthropogenic emission sources within the Montréal area. Similar regional emissions are also evident from the geographical patterns of the 50 and 25 μeq L^{-1} SO_4^{2-} and NO_3^- isopleths over the Abitibi-Témiscamingue (N-W) and Saguenay - Lake St. John (N-Central) region.

In order to estimate accurately the wet deposition rates of atmospheric pollutants in the province, we have to remember that the CANSAP sampling stations are mostly located at airports where most of the Canadian Atmospheric Environment Service Weather Observation stations are in operation. It is thus evident that a part of the measured deposition of atmospheric pollutants within the St. Lawrence Lowlands originates with regional and local emissions and that one cannot extrapolate regional values directly to remote areas such as the Laurentide Park. Although local emissions, regional and long-range transport of material are difficult to differentiate and quantify, Lewis et al. (1983), by studying the snow composition of different storm events within the Montréal region, concluded that the urban emissions add a significant amount to the chemical load of air parcels moving through the region. On the other hand, their study also confirmed the existence of the long-range transport of atmospheric pollutants. Back tracking of air trajectories showed that air parcels which had passed over SO_x and NO_x emission sources to the west and southwest (Ontario - Great Lakes Region) gave snowfalls which had lower pH values and higher concentrations of sulphate and nitrate than average. Singh and Nobert (1982), in their study dealing with the chemical caracteristics

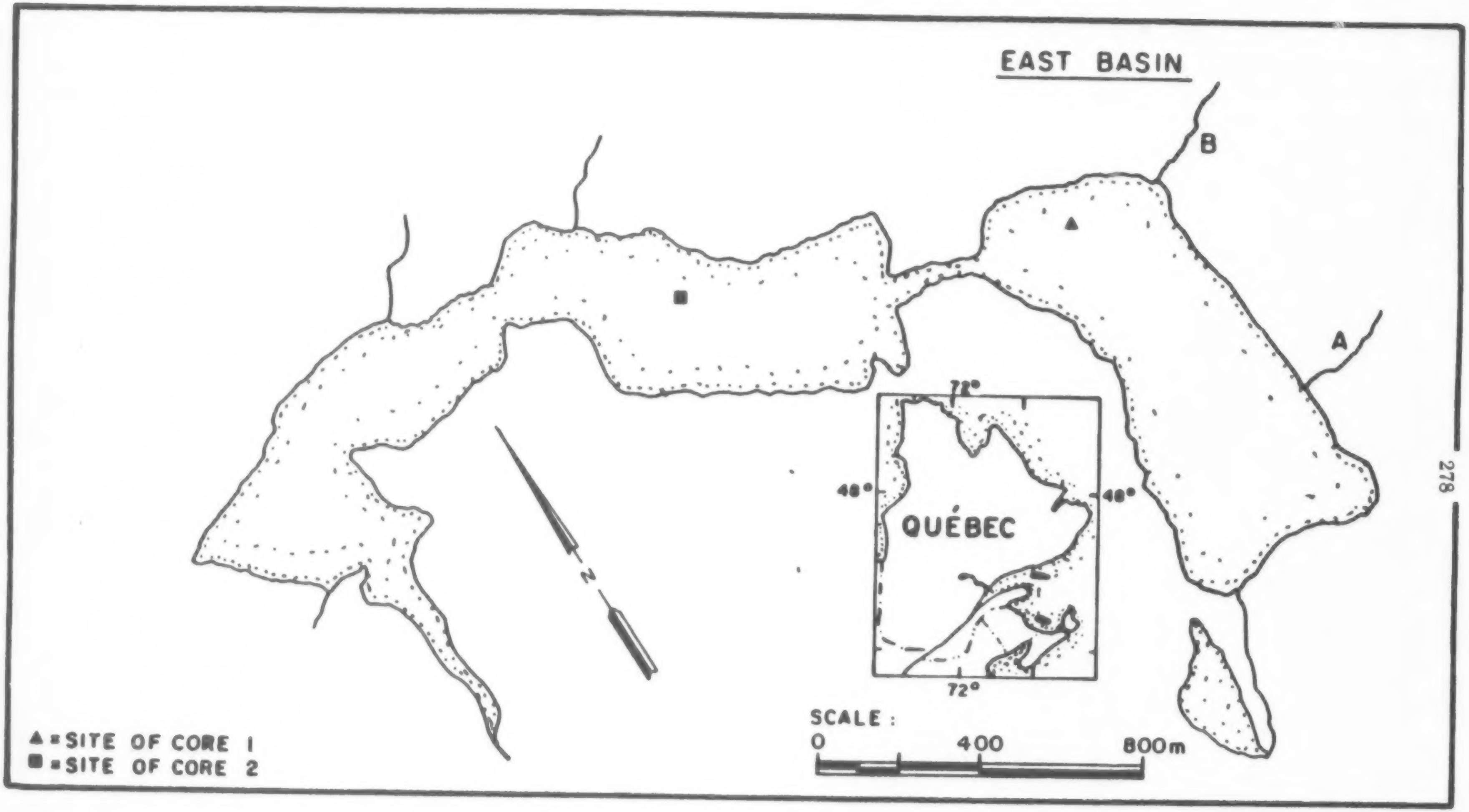
EAST BASIN
B
A
QUÉBEC
72°
48°
48°
72°
N
SCALE :
0
400
800m
▲ = SITE OF CORE 1
■ = SITE OF CORE 2

Figure 6. Lake Tantaré morphological characteristics and studied sites (Δ - site of core 1; ▪ - site of core 2).

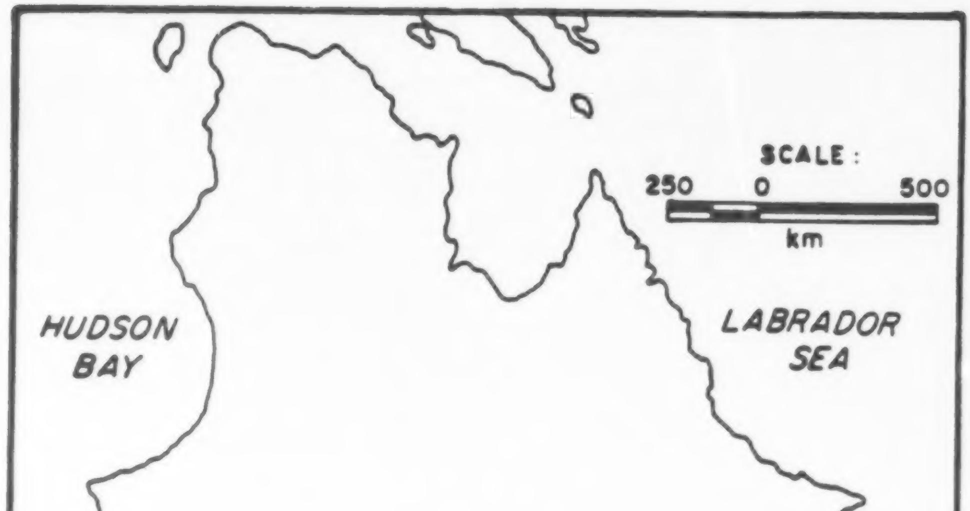
SCALE :
250
0
500
km
HUDSON BAY
LABRADOR SEA
10
50
70
GULF OF ST·LAWRENCE
N.FLD
N.B
USA.
ONT.

Figure 7. Spatial distribution over the southern part of the Province of Québec of the mean SO_4^{2-} concentration (μeq L^{-1}) of the wet precipitation for the period of June 1981 to the end of January 1982 (PQPN data).

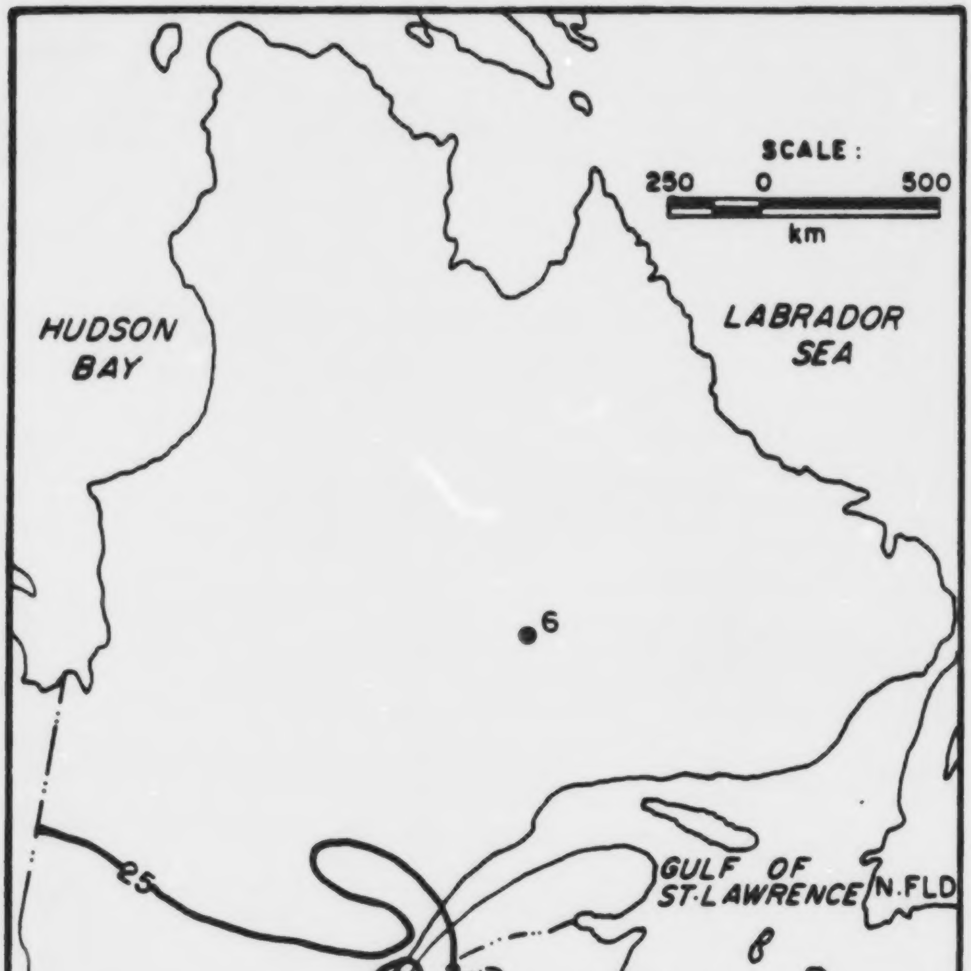
SCALE :
250
0
500
km
HUDSON BAY
LABRADOR SEA
6
25
30
GULF OF ST·LAWRENCE
N.FLD
N.B
ONT.
USA.

Figure 8. Spatial distribution over the southern part of the Province of Québec of the mean NO_3^- concentration (µeq L^{-1}) of the wet precipitation for the period of June 1981 to the end of January 1982 (PQPN data).

of the precipitations in the James Bay region, also came to the same conclusion relative to the origin of most acid precipitation events. Lachance et al. (1977) detected the effects of the regional chemical loading originating from the Montréal region on the quality of the precipitation within the Québec Eastern Townships localized about 100 km southeast of Montréal.

By comparing the chemical composition of the CANSAP data obtained at the Québec Airport to the data of other networks (CAPN, PQPN), it can be shown that although the concentration of Ca^{2+} ions is higher at the Québec Airport by factors of 7 and 3 for the 1977-1981 and 1981 data, respectively, the concentration of H^+ ions in the first set of data (1977-1981) is of the same order as that found at remote sites within the Laurentides Park. The higher concentration of H^+ ions for the 1981 CANSAP data might be attributable to the siting and sampling error as discussed by Barrie and Sirois (1982). We also have to note that composite sampling was initiated in January 1980.

Seasonal trends

Precipitation chemistry, which is a complex result of various terrestrial and atmospheric processes (Fowler 1980), varies not only as a function of space but also as a function of time. The quality of the wet precipitation is highly dependent on the season, and meteorological conditions. In order to identify the seasonal behavior of the quality of the precipitation in the Laurentides Park, we used the mean monthly concentrations from the 1981 CAPN station at the Montmorency station (Table 1). The seasonal behavior of the precipitation components exhibited marked trends and is illustrated in Figure 9. These trends and other less dominant ones are also well established in the correlation matrix (Table 4) which shows a significant positive regression ($p<0.01$) between H^+ and SO_4^{2-}, NH_4^+ and SO_4^{2-} and a less strong positive correlation coefficient ($p<0.05$) between the mean monthly air temperature and SO_4^{2-}.

The dispersion of the values around their annual mean clearly shows the winter season importance of Cl^-, NO_3^-, K^+, Na^+, Mg^{2+} and Ca^{2+}, which are listed in a decreasing order of relative importance. The significant negative correlation coefficient (-0.71) between the Cl^- and temperature ($\rho<0.01$) and between the NO_3^- and temperature ($\rho<0.05$) reflect their more important abundance during the winter season. Some of the NO_3^- may originate from the additional combustion of petroleum fuels during this period, whereas the increases in Cl^- concentration can be attributed to the local application of road salts. The significant ($\rho<0.05$) relationship between Cl^- and Na^+ is probably another indication of the contamination of the wet precipitation at the Montmorency CAPN station by road salt. Grimard (personnal communication, 1983) also found contamination originating from the same source at the Mont-Apica PQPN station. It is well known (Munger 1982; Raynor and Hayes 1982) that various seasonal activities (such as heating, plowing) or natural events (such as mineral particles derived from the ground surface in the spring or from the snow in winter) affect the seasonal quality of the precipitation.

From the above discussion it is evident that local and regional contaminations of a seasonal nature, as well as the inadequate siting of many CANSAP stations, can lead to errors (mostly overestimation) in chemical deposition rates. Hence, we believe that the long-range atmospheric pollutant loadings over the Laurentide Park, estimated from the CANSAP data since 1977, have been overestimated and that some portion represents the regional and local emissions at the sampling sites.

Regional Chemical Limnology

There exist many investigations indicating that anthropogenic acidic-pollutants such NO_x and SO_x have contributed to the acidification of surface waters in remote areas of Norway (Braekke 1976; Wright and Henriksen 1978), Sweden (Hörnström et al. 1973; Oden 1976; Dickson 1975), Scotland (Wright and Henriksen 1980), the northeastern United States (Schofield 1976; Davis et al. 1980), Ontario (Conroy et al. 1976), Québec (Jones et al. 1980; Bobée et al. 1982; Richard 1982) and Maritime Provinces (Watt et al. 1979.

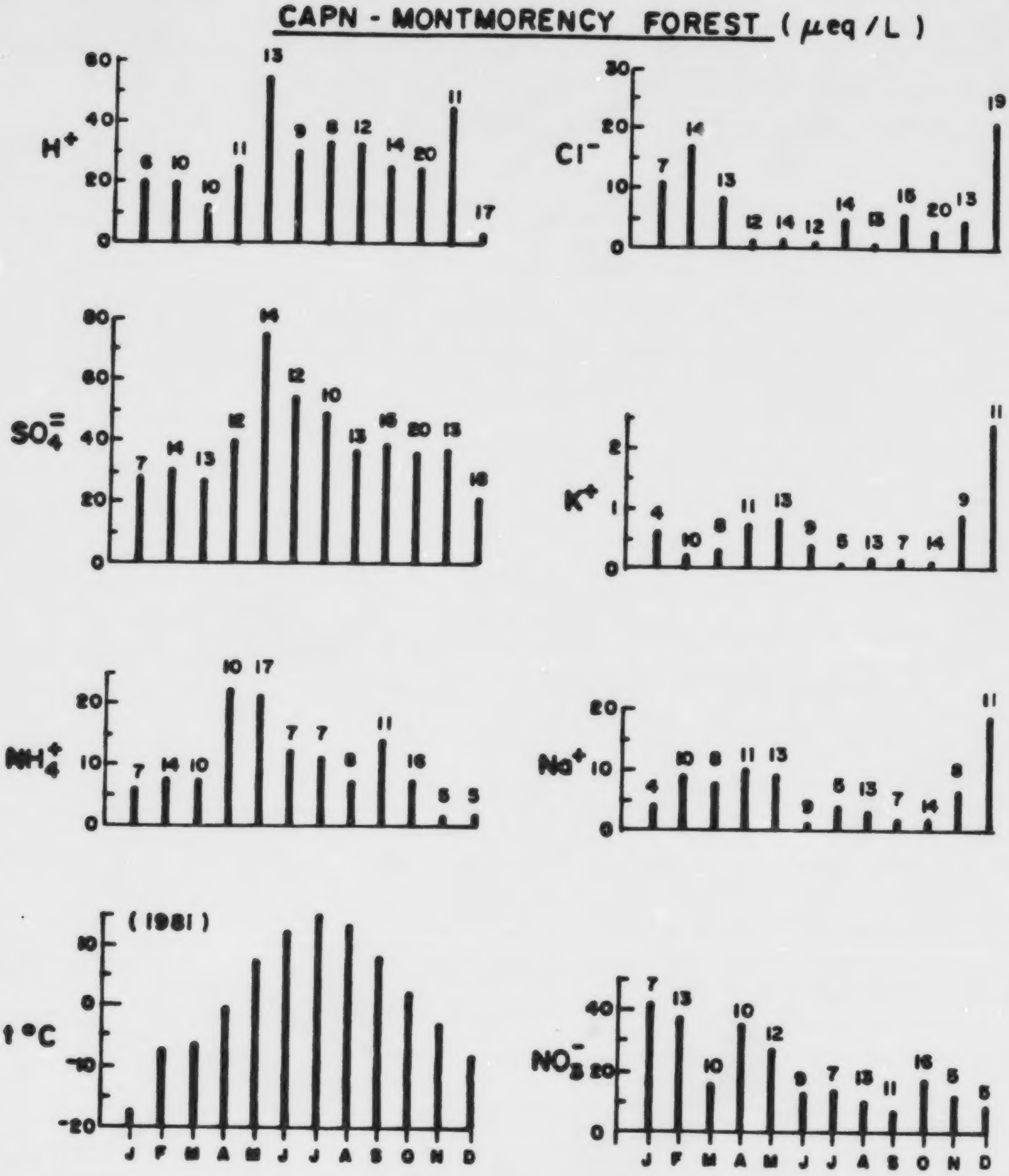

Figure 9. Monthly average distribution of H^+, SO_4^{2-}, NH_4^+, Cl^-, K^+, Na^+ and NO_3^- concentration (μeq L^{-1}) in the precipitation for the year 1981 at the Montmorency Forest monitoring station of the Canadian Air and Precipitation Network (data compiled from Barrie et al. 1982) and monthly mean air temperature in °C.

Table 4. Correlation matrix of the monthly average chemical composition of precipitation for the 1981 CAPN - Montmorency Forest station

	H^+	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	NH_4^+	Mg^{2+}	Na^+	K^+	ppt	t°C
H^+	1	0.83++	0.0	-0.70++	0.18	0.42	0.17	-0.32	-0.35	-0.09	0.52
SO_4^{2-}		1	0-.01	-0.66+	0.25	0.70++	0.21	-0.20	-0.23	0.05	0.63+
NO_3^-			1	0.16	0.45	0.28	0.36	-0.02	-0.10	0.12	-0.55+
Cl^-				1	0-.11	-0.54	0.08	0.57+	-0.58+	0.05	-0.71++
Ca^{2+}					1	0.47	0.94++	0.47	0.46	-0.25	-0.20
NH_4^+						1	0.28	-0.09	-0.28	0.21	0.44
Mg^{2+}							1	0.63+	0.64+	-0.25	-0.31
Na^+								1	0.80++	0.06	-0.33
K^+									1	-0.31	-0.45
ppt										1	0.19
t°C											1

+ significant at $p < 0.05$

++ significant at $p < 0.01$

The acidification and accompanying environmental chemical changes on surface waters low in minerals are complex and not well understood. Strong pH toxicity, especially associated with snowmelt or heavy autumn rains, has been recorded (Leivestad and Muniz 1976; Leivestad et al. 1976; Farmer et al. 1981). In addition, when pH is decreased, toxic metals are mobilized and leached from the lacustrine sediments or from the watershed (Pionke and Corey 1967; Cronan and Schofield 1979; Johnson 1979; Norton and Hess 1980; Schindler et al. 1980). Changes in Atlantic salmon rivers have also been documented; Van Coillie et al. (1982) observed greater concentrations of Al, Fe and Cu in the lower reaches of four Québec Atlantic salmon rivers, and Watt et al. (1983) showed decreased HCO_3^- concentrations and increased Al and SO_4^{2-} levels in Nova Scotian rivers. The proportion of acidic substances and metals originating from the catchment relative to the quantity in atmospheric fallout is difficult to evaluate. Likens et al. (1977) showed in a watershed mass-balance study of Hubbard Brook that 32% of the S inputs to the system are of dry origin. Ouellet and Jones (1983) showed that atmospheric Pb inputs to the aquatic system are important even for lakes localized in the remote Québec Ungava region.

Most other regional studies in Québec have focused on the change of water quality using multivariate techniques. An analysis of earlier data obtained from various monitoring programs (Bobée et al. 1982) revealed a number of inconsistencies between fixed-point alkalinity determinations and those calculated from pH and dissolved inorganic carbon, which led to total inflection-point alkalinity determinations and other methodological refinements. From an analysis of 256 lakes, the most revealing discoveries were that 1) lakes on the Canadian Shield were far more sensitive to acidification than those on the Laurentian lowlands and 2) a pronounced southwest to northeast gradient of decreasing sulphate concentration was present in Shield lake waters, suggesting that the distribution of sulphates was controlled by atmospheric processes rather than by any localized geological sources.

Studies in more restricted geographical areas on the Shield conducted by the present authors (unpublished) revealed similar results; a study on 110 lakes within the Laurentides Park showed that most lakes had a low buffering capacity.

From a statistical R-mode factor analysis of the various topometric, morphological and physicochemical data available for the lakes studied (Fig. 10), a tendency is seen for the more acid lakes to be distributed within the southwestern part of the Park (high positive longitude loading in relation to the high negative one of H on factor F2,) which agrees with the findings of Jones et al. (1980) and is similar to those of Bobée et al. (1982). Thus, this part of the study area is probably receiving more atmospheric pollutants originating mostly from the Great Lakes - St. Lawrence Valley because of the orographic effect of the Laurentide Plateau on the air masses moving dominantly in a N-E direction. In contrast, the grouping of total inorganic carbon (TIC), Mg, alkalinity, latitude and pH of the 110, lakes was attributed to those lakes lying on the more calcareous glacial deposits present in the northwestern part of the Park, as well as to the less sensitive ones located mostly at lower elevations. The watershed/lake surface ratio (B/L) seems also to be an important variable in these less sensitive lakes. They are characterized by a low transparency which may be the result of higher productivity in the pelagic waters. We must note, however, that highly colored lakes (color >40 units) were eliminated from the statistical treatment. Finally, we were unable to find a strong correlation ($p<0.01$) between pH and aluminum. This is similar to the results of Bobée et al. (1982) but unlike those of Richard (1982) or Campbell et al. (1983).

Richard (1982) carried out a series of comprehensive studies employing both physicochemical data and fishery yield/effort statistics to evaluate if a decrease in fish population could be attributed to lakewater acidification. Only slight decreases in yield in the more acidic lakes were demonstrated, and it could not be unequivocally stated whether these were related to acidic conditions or to differences in the fishing intensities in individual lakes.

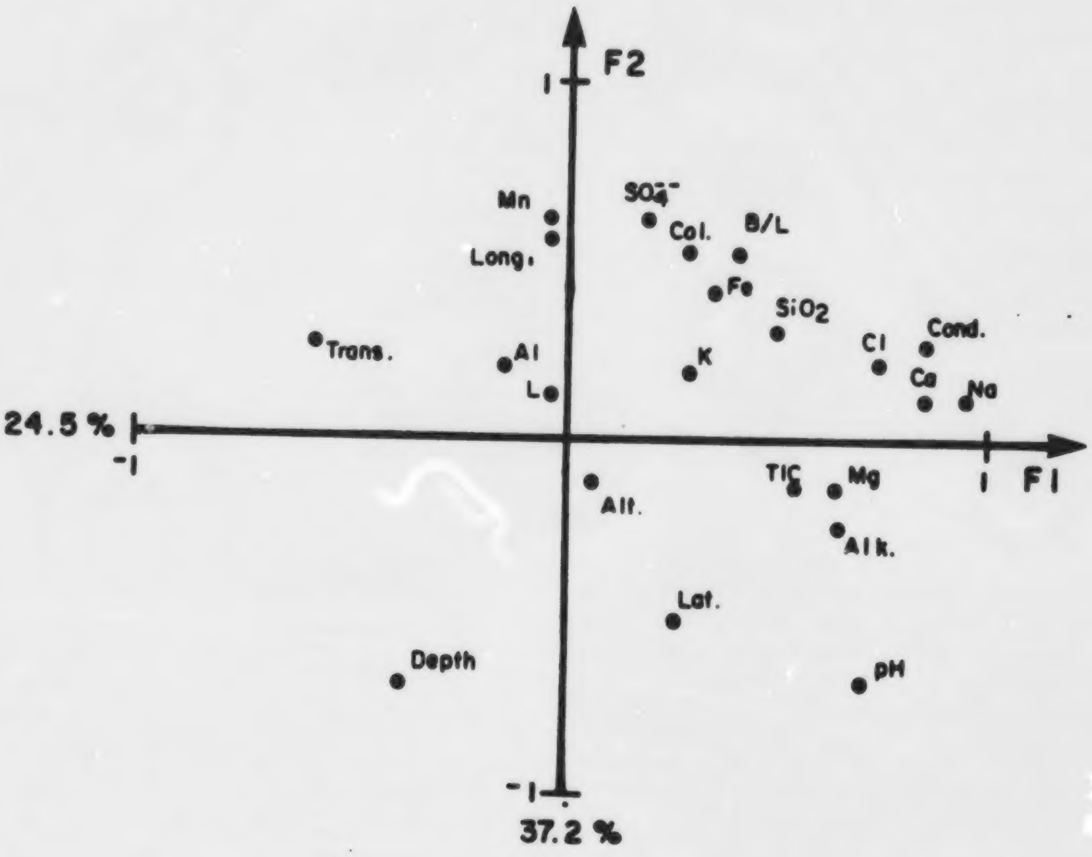

Figure 10. Scattergram of the loadings on the two first factors of an R-mode multivariate statistical analysis of various topometric, morphological and physicochemical data of 110 lakes studied in the Laurentides Park (data from Ouellet et al., unpublished) (trans. = secchi disc transparency; long. = longitude of the lake; lat. = latitude of the lake; col. = color; cond. = conductivity of the water; B/L = watershed/lake area).

Generally, attempts to unveil mechanisms from these types of descriptive data have not been as successful as experimental approaches carried out elsewhere in Canada (Schindler et al. 1980; Dillon et al. 1979; Yan et al. 1982).

Our work has focused mainly on Lake Tantaré and Lake Laflamme, which we consider good representatives of acidified and non-acidified environments respectively in the Laurentide Park. Lake Tantaré has higher concentrations of H^+, SO_4^{2-}, NO_x^-, K^+, Al^{3+}, Fe and Mn (Table 3) and a greater water transparency ($e = 0.2\ m^{-1}$), similar to other acidic lakes on the Canadian Shield.

Lake Tantaré Experimental Watershed

Throughfall

The Lake Tantaré watershed is fully forested but the quality of throughfall, (Table 3) has only been examined in the mature yellow birch stands on the eastern shoreline (facing southwest) of the shallow basin (Jones et al. 1983). This arborescent association, although not representative of the whole watershed, covers the major part of the drainage area of two streams (Fig. 6). Of these streams, one (B) shows consistently low pH values (4.4-4.6) whereas the second (A), which is of relatively very minor importance in the hydrological system, is not so acid (pH 5.8-6.2).

Yellow birch throughfall quality varies greatly with the season, rain intensity, quality of the incident precipitation, number of rain-free days before an event and tree species (Eaton et al. 1973). The result of all these factors is that annual variations in the quality of throughfall can be greater than in the incident rain. This is particularly true if throughfall quality is followed from spring through to late summer. However, certain general conclusions can be reached based on mean seasonal values for throughfall, when the effect of the canopy on the incident precipitation reaching the soil is greatest (spring) or least (autumn).

Table 3 shows the mean seasonal incident rainfall quality and the throughfall quality in spring and early summer 1982. The high neutralizing capacity of the yellow birch canopy towards the incident precipitation during this period is demonstrated by the removal of over 97% of the incident hydrogen ion concentration which is replaced by calcium, magnesium and particularly potassium ions. In addition, a comparison of the sum of cations in rain and throughfall shows quantities of calcium, magnesium and potassium greater than those necessary to neutralize the quantities of hydrogen ion in the incident precipitation. In autumn, when leaves are falling or have fallen, throughfall acidity is frequently higher than that of the incident rain. These differences demonstrate the active participation that the metabolic processes of tree and leaf play in the removal of hydrogen ions at the atmosphere-canopy interface. The results for birch throughfall at Tantaré are in agreement with those noted by Eaton et al. (1973) and Abrahamsen et al. (1977), although concentration values for different ions vary in each case presumably due to the location of the individual sites.

For strong acid anions the total anionic content of incident rain and throughfall increases for all rain events in the case of SO_4^{2-} but remains relatively stable or decreases for NO_3^- according to the individual event.

At present these results cannot be extrapolated for acid deposition over the entire watershed (per annum) as these conclusions are based on mean values for certain rain events during the period of spring to early autumn 1982 as calculated from data obtained during sequential sampling during the individual events (Jones et al. 1983). Greater or lesser variation in throughfall and rainfall quality may be observed during periods when losses or gains of anions derived from strong acids fluctuate irregularly around the mean values. Moreover, as SO_4^{2-} deposition increases in throughfall are due primarily to the washoff of aerosols deposited during dry periods, SO_4^{2-} increases may be related to the capture efficiency of the canopy. Thus, the contribution of dry deposition to total SO_4^{2-} deposition should be more evident in that part of the Tantaré watershed containing spruce trees. These and other conifers are known to have less neutralizing effect on incident rain than birch due mainly to their higher interception rates of wind-borne aerosols during dry periods and subsequent washoff (Abrahamsen et al. 1977). It is thus possible that in the watershed, total acid deposition on the ground may be closer to, or even greater than, the incident precipitation if acidification of rainfall by conifer canopy contact exceeds the neutralizing capacity of hardwoods in the spring and early summer.

In this context caution is necessary in relating the quality of yellow birch throughfall to the stream and lake waters. However, it is significant that the very acidic nature of the major stream (B) running through the birch stands and entering the first basin of the lake on the eastern shore is very little influenced by throughfall quality in either spring (pH = 5.95) or autumn (pH = 4.2). Values of pH for the stream in both spring rains (after the spring snowmelt has been flushed out) and autumn rains is approximately 4.6. Anionic composition (Table 3) of these running waters is completely dominated by SO_4^{2-} which has displaced to all intents and purposes the bicarbonate ion as a major anion. Cation concentrations show evidence for the geological leaching of calcium and sodium from the soil or subsoil matrix while magnesium and potassium are retained by the watershed. Although the streamflow responds rapidly to rain episodes, stream quality cannot be related directly to the quality of throughfall because the residence time of water in the different subsoil levels that feed the streams is not known. Depending on both the surface water and groundwater flow patterns, precipitation entering the watershed may simply displace groundwater towards the stream or beds, alternatively, may move more rapidly, with some groundwater, through the thin soil cover into the drainage system. In the latter case, relatively greater exchange rates of ions and elements between incident precipitation plus throughfall and soil plus subsoil would be necessary to account for the difference in stream and throughfall quality. This is particularly true in the case of aluminum, which with manganese shows the most striking concentration changes in these waters as compared to precipitation and throughfall. Manganese concentrations are relatively high in throughfall compared to those found in the streams and demonstrate the large quantities of this element which are cycled in the forest system. In contrast, very little aluminum seems to be recycled, but large quantities are mobilized during the passage of precipitation through the substrata towards the streams. The mobilization of aluminum ($\sim 350\ \mu g\ L^{-1}$) into these waters sets up stress conditions (Baker and Schofield 1982) for the fish population which at present is regressing (Frenette 1984). The mobilization of aluminum in soil and groundwater becomes appreciable at a pH of below 5; above this value aluminum ions tend to precipitate out of solution as colloidal complexes. In lake waters this leads ultimately to the floculation and aggregation of larger particles and their transport to the sediments. This mechanism could account for the increase in Al in the most recent sediments (0-10 cm) of the eastern basin (Fig. 11).

This could also be the explanation for the lower concentrations of aluminum found in the waters of the first basin of the lake (mean pH value, 5.1 = 7.94 $\mu eq\ H^+\ L^{-1}$, Table 3). This decrease in the acidity of the lake waters, as compared to the tributaries, is due mainly to an increase in calcium concentration (50 - 75 $\mu eq\ L^{-1}$) resulting from the contact between lake waters and sediments during the residence time of the former in the shallow lake basin. The ionic composition of the lake waters is more closely balanced than that of throughfall or streams. The anionic deficiencies in both the latter waters are probably due to material of an organic acid nature (Jonsson 1977) which, from the ionic balance in the lake water, appear to be selectively removed in the lake by sedimentation or metabolic processes.

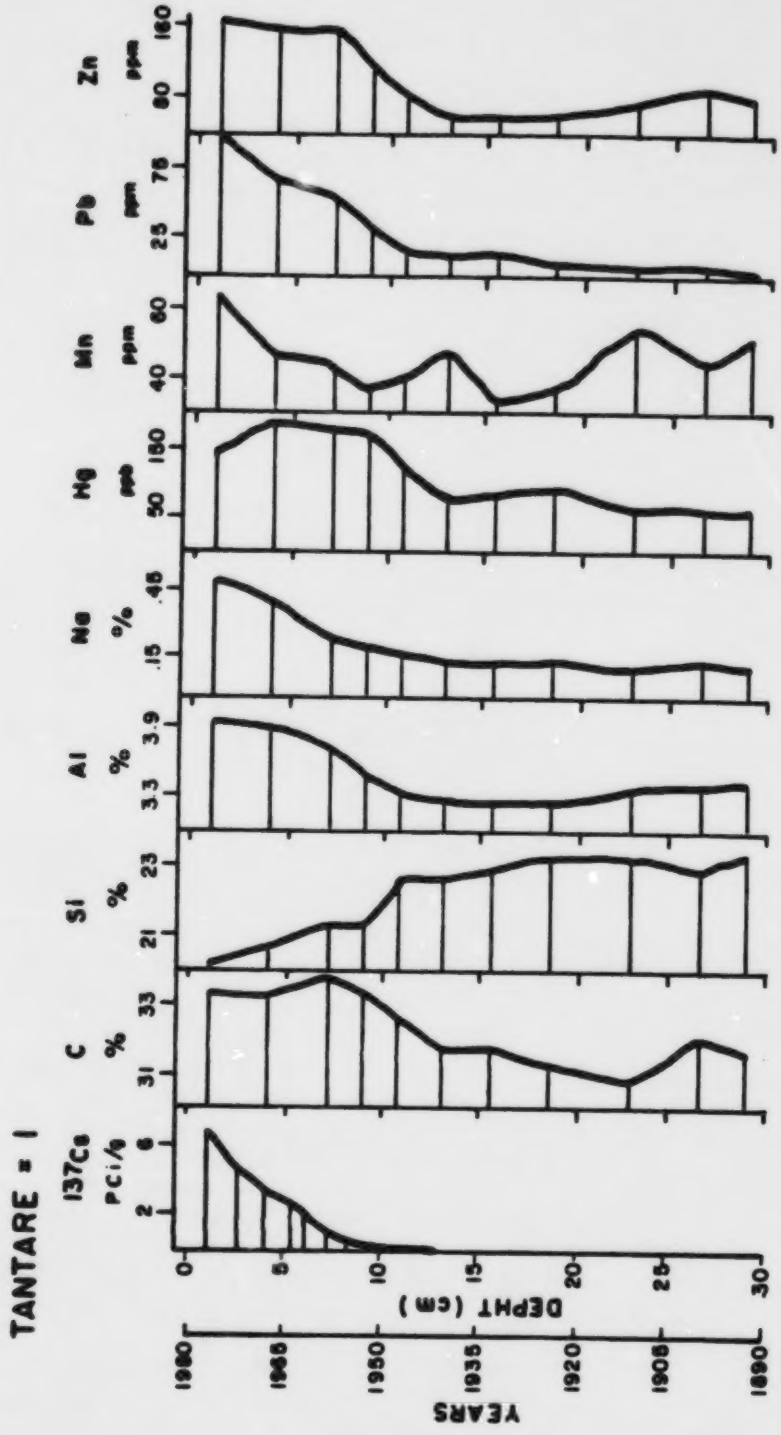

Figure 11. Stratigraphical distribution of some geochemical variables in the most recent sediments of the eastern basin of Lake Tantaré.

Lacustrine sediments

Considerable effort has been recently devoted to obtaining historical records of the chemical composition of atmospheric pollutants and their effects in the Northern Hemisphere through the analysis of the successively dated lacustrine sediment horizons (Davis et al. 1980; Norton and Hess 1980; Ouellet 1981; Ouellet and Jones 1983). Although it is generally accepted that chemical constituents originating in solution or in suspension from the watershed will be concentrated in the lacustrine sediments, the preservation of these is highly dependent on the limnological characteristics of the receiving water body, as well as on the individual chemical dynamics of each constituent. Ouellet and Jones (1983) have recently shown that the stratigraphic behavior of some heavy metals, mostly of atmospheric origin (Pb, Hg, Zn), in lacustrine sediments was quite similar for an acid and non-acid lake and responded to anthropogenic influences. However, other variables such as Al and Mn will have a different stratigraphical distribution in these two different types of lakes. In order to shed light on the behavior of geochemical parameters of lake sediments subjected to acidic inputs we have studied sediment cores sampled from the deepest point of the eastern thermically unstratified shallow basin (Fig. 11) and from the second deepest stratified basin (Fig. 12).

Based on the stratigraphic distribution of ^{137}Cs, the rate of sedimentation was calculated to be approximately 3.3 mm yr^{-1} in both basins. Based on their recent stratigraphic behavior (Figs. 11 and 12), the other geochemical variables are divisible into three groups. Concentrations of ^{137}Cs, C, Na, Hg, Pb and Zn are all increasing from about the 10- to 20-cm stratigraphic interval upward in both cores. The subsequent reduction in the stratigraphic concentration of Zn, Hg and, to a lesser extent, Pb has recently been attributed to the important decrease, since 1960, in the total particulate emission to the atmosphere associated with new antipollution technologies (Ouellet and Jones 1983). The slight increase of total C, by about 2%, during the last 30 years in both basins of Lake Tantaré might be another indication of its recent trend in acidification. It has been shown by several authors (Grahn et al. 1974; Laake 1976) that decomposition of organic matter is reduced in acid lakes, there being a general shift from a bacterial to a fungal decomposer community. One of the most typical features of an acid lake such as Tantaré is the accumulation of large quantities of organic debris, plants (Isoetes), twigs along the shores; this phenomenon has been noted by other workers (Grahn et al. 1974). The typical mat of coarse detritus, fungi and algae on top of the sediments described by these authors is also present in Lake Tantaré. A consequent reduction in the microbial activity of Lake Tantaré, which would greatly affect the availability of nutrients, might then explain its poor phytoplanktonic community and its unusually great Secchi-disc transparency of 11.0 m, as discussed for Norwegian acid lakes by Almer et al. (1978). The changes in these lakes brought about by the acidification of their surface water have led Grahn et al. (1974) to formulate a hypothesis of oligotrophication of the lacustrine system. The recycling of nutrients by the action of bacteria (Traaen and Laake 1980) is another important mechanism which is highly affected in acid aquatic environments and needs further investigation.

The second stratigraphic behavior pattern is represented by Si which is characterized by a marked diminution at the 10-cm level in both cores. This negative response to the impact of acid precipitation is the consequence of the oligotrophication of the system in which the diatom community has been greatly reduced. The absence of these siliceous organisms would then contribute to the substantial lowering of the biogenic silica. This explanation is supported by the work of kickman et al. (1981) who by the use of fossil diatoms have demonstrated a recent reduction of pH in Lake Tantaré.

The third group of sedimentary chemical substances, which is composed of Al and Mn, exhibits opposite stratigraphic trends in both cores. They increase toward the top of the sediments in the first basin but decrease within the 0- to 10-cm interval of the second deeper basin. The increased leaching of these elements from the watershed at lower pH (Gjessing et al. 1976; Cronan and Schofield 1979; Van Coillie et al. 1982) is also supported by the surface water chemistry of the inflowing water as discussed above. The present results suggest that the elements mobilized at pH values near 4 within

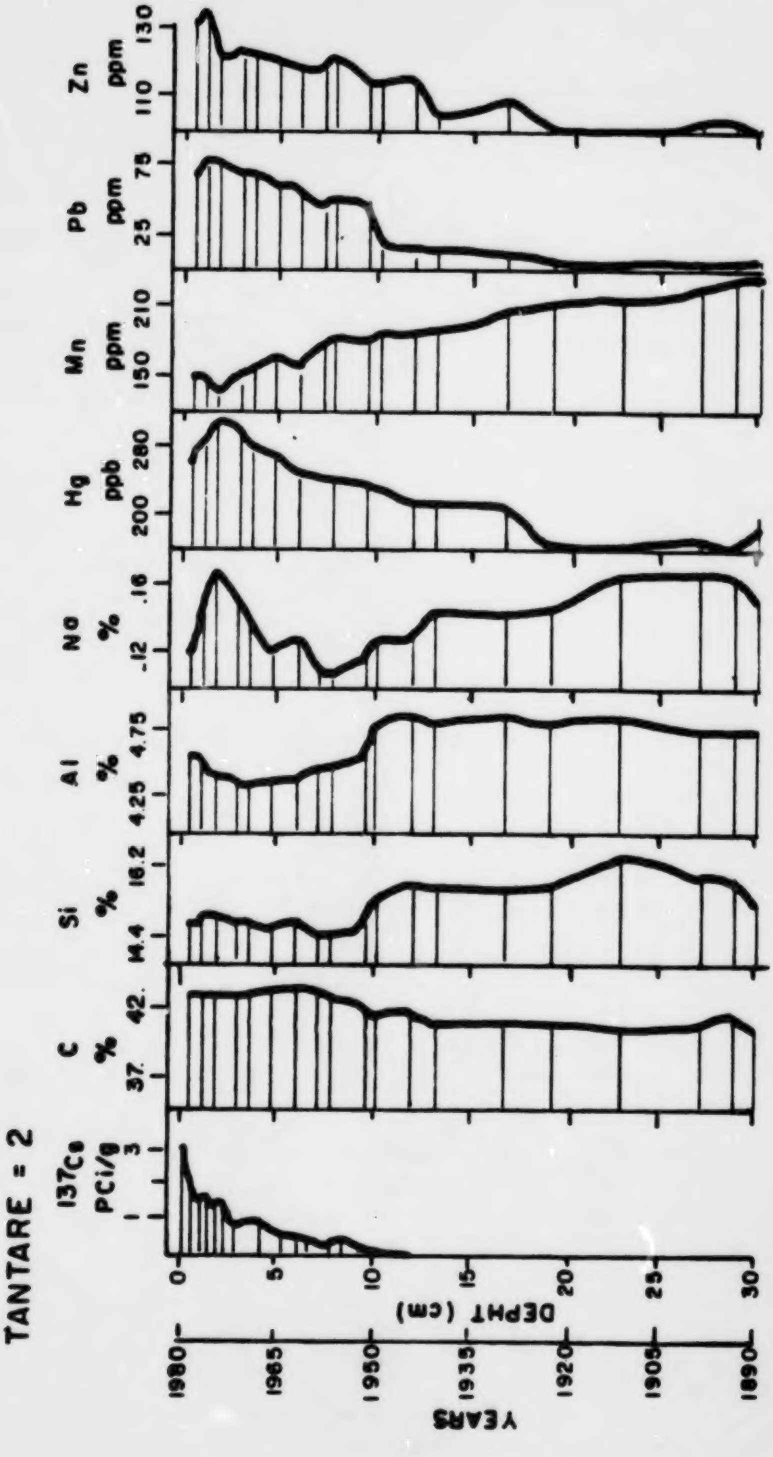

Figure 12. Stratigraphical distribution of some geochemical variables in the most recent sediments of the second basin of Lake Tantaré.

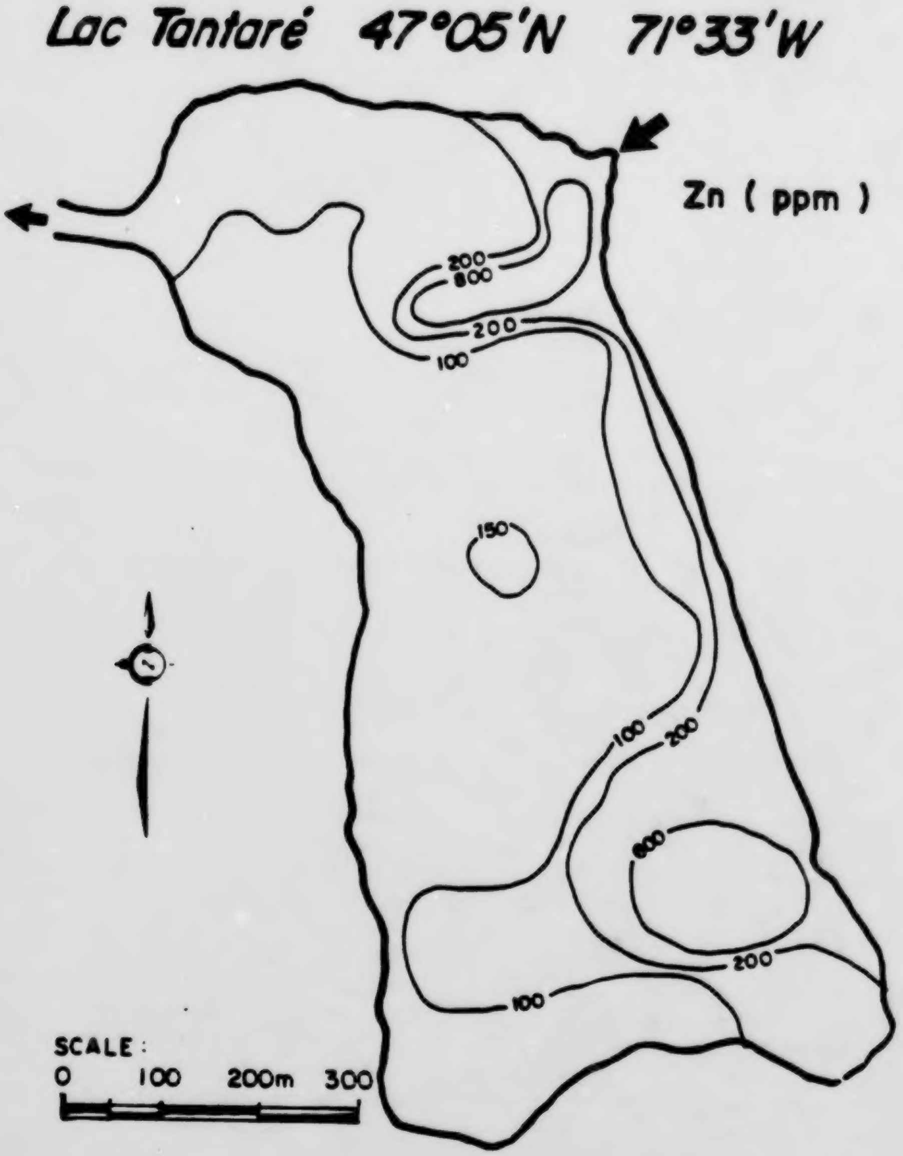
Lac Tantaré 47°05'N 71°33'W
Zn (ppm)
200
800
200
100
150
100
200
800
200
100
SCALE :
0
100
200m
300

Figure 13. Distribution of Zn in the surficial sediments of the eastern basin of Lake Tantaré.

the watershed and transported by the surface running waters to the lake compartment (average pH 5.1) are then in part, especially for Al, reprecipitated within the shallow eastern basin. On the other hand, and especially for Mn, the opposite trends observed in the stratified deeper basin are most likely associated with the lower pH of the hypolimnic water as well as the winter and late summer anoxic reducing condition. These elements are then remobilized at the water-sediment interface and pass out of the lacustrine system.

As far as the time scale of the various events is concerned, it is interesting to note that for both cores Hg, Pb and Zn start to increase slowly, especially for the second basin, close to the 20-cm stratigraphic level. On the other hand, stratigraphic changes for C, Al, Na and Si become clearly evident only at the 10-cm level. From our ^{137}Cs dating results we interpret the first slight changes of Hg, Pb and Zn, below the 10-cm level, as the first indicator of long-range atmospheric transport of pollutants which appeared to date back to the early 1920s. Then and up to about 1950, the impact of acidifying products on the Tantaré aquatic systems was most likely minor. But close to the 1950s drastic changes appeared within the whole system. These were probably the results of the larger atmospheric pollutant influxes derived from coal combustion, which peaked shortly after the war (Perry 1983), as well as the gradual loss of the buffering capacity of the whole system (terrestrial and aquatic).

The geochemical study of 35 surficial sediment samples distributed over the entire eastern basin of Lake Tantaré has revealed an important source of Zn originating from the watershed via creek B located in the N-E corner (Fig. 13). A promontory from the mouth of the creek toward the deeper water, which corresponds approximately to the deltaic area of the creek, is characterized by Zn levels reaching 800 ppm, which are about four times higher than the average concentration of the whole lake water - sediment interface. A similar high Zn level, but reaching 600 ppm, is also found close to the inflow of creek A. The shallower water at that end of the lake, as well as its greater exposure to northern winds, are probably responsible for the wider spatial distribution of the Zn anomaly. These distributions are unusual and do not correspond to the finding of Ouellet and Poulin (1977) and Ouellet (1980), who have shown that in surficial lake sediments Zn is strongly positively correlated ($p<0.05$) with water depth. Heavy metals are preferentially bound to the finer particles which are gradually transported by hydrodynamic forces, acting within the water body, toward the deepest point of the lake where they settle preferentially.

The recent anomalous Zn distribution in the surficial lake sediments by the mouth of creek B of Lake Tantaré is supported by the stratigraphic distribution of that element as discussed above. From our ^{137}Cs-dated geochemical diagram this phenomenon appears to have been initiated in the early 1950s, which agrees with the findings of Cogbill and Likens (1974), Cogbill (1976) and Likens and Butler (1981) regarding the historical evolution of the pH of rain in northeastern America. The marked acidification of the precipitation since the 1950s, as established for Québec by Ouellet and Jones (1983), would then have contributed to the mobilization of Zn from the watershed, especially at pH values of about 5. The Zn would enter the lake through the creek water (pH 4.6) and then be partly reprecipitated as it reached the lake water of pH 5.1.

Although Al is well known to be strongly mobilized from the watershed at pH values below 5, its spatial distribution in the surficial sediments of the eastern basin of Lake Tantaré (Fig. 14) does not show any anomaly such as that of Zn. Its maximum abundance is found away from the shore where finer and lighter particles settle preferentially to the lake bottom. The general distribution of Al relative to that of Zn is most probably also related to the critical mobilization-flocculation found at pH levels of about 5. As this critical pH level is also that of the lake into which the creek flows, a strong retention of this element within the lake basin is not possible. This loss of Al from the lake systems is well supported by the marked reduction of Al within the 0- to 10-cm core interval of the second basin (Fig. 12).

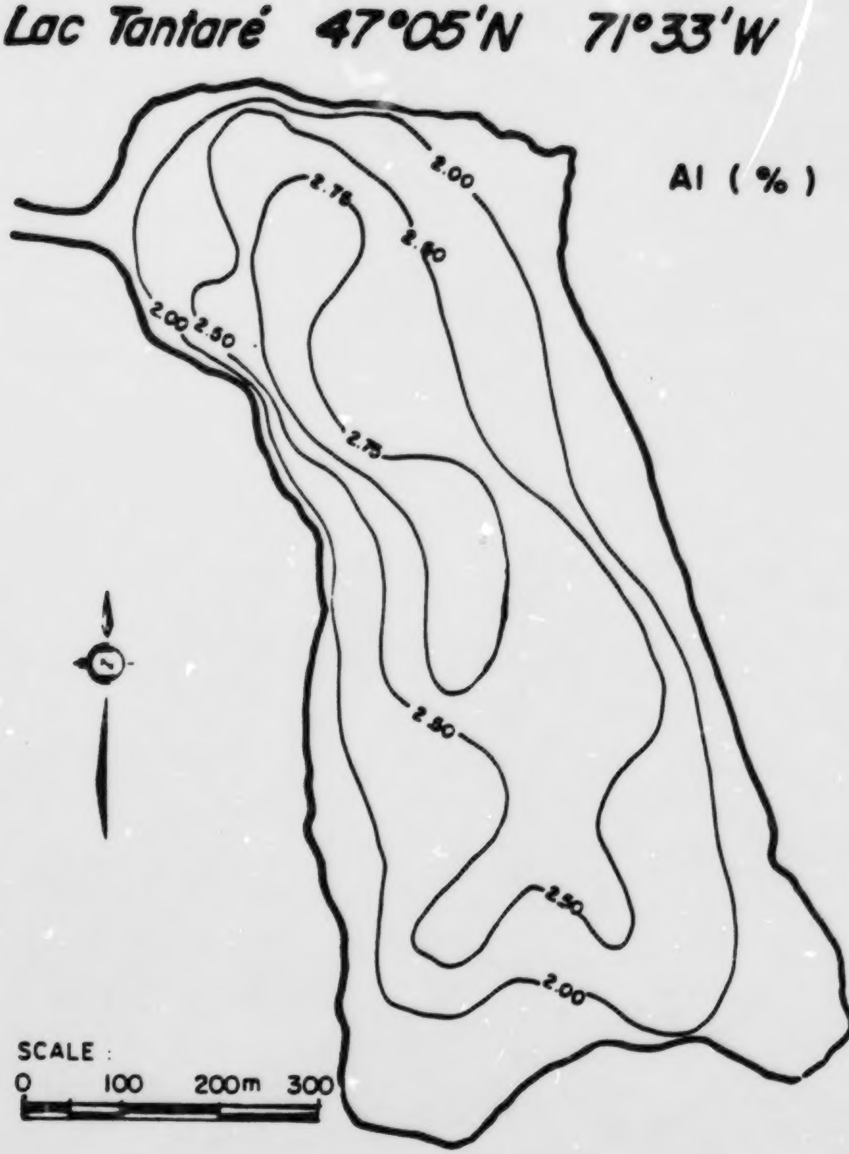
Lac Tantaré 47°05'N 71°33'W
Al (%)
2.00
2.75
2.50
2.00
2.50
2.75
2.50
2.50
2.00
SCALE :
0 100 200m 300

Figure 14. Distribution of Al in the surficial sediments of the eastern basin of Lake Tantaré.

CONCLUSION

Our study has shown that the chemical composition of precipitation falling over the Laurentide Plateau of the Precambrian Shield north of the St. Lawrence Lowlands, as estimated since 1977 by CANSAP, has been overestimated for most of the parameters. The CANSAP data are a combination of local, regional and long-range atmospheric inputs. Although this precipitation sampling network is now being replaced by new Canadian (CAPN) and provincial (PQPN) networks appreciably less susceptible to local and regional anthropogenic inputs, road salt contamination is still evident in the new networks.

Within the Laurentides Park, except for the northwestern area which is geologically more calcareous, the spatial distribution pattern of the acid lakes is difficult to establish. Susceptibility to lake acidification is the result of several interrelated factors such as topography, morphology, geology, vegetation cover and the chemistry of the various components, this result varying for each lacustrine system.

As the atmospheric waters flow through the various hydrological compartments of the Tantaré watershed (Fig. 15), all chemical constituents are substantially increased except for H^+ and NO_x. Concentrations of Ca and Al in the lake sediments of the first basin of Lake Tantaré are respectively 17 000 and 4 x 10^6 times higher than in the incident precipitation.

Stratigraphic and surficial geochemical studies of lake sediments are powerful tools toward understanding the historical impact of acid rain on lakes which are intimately linked with their watersheds.

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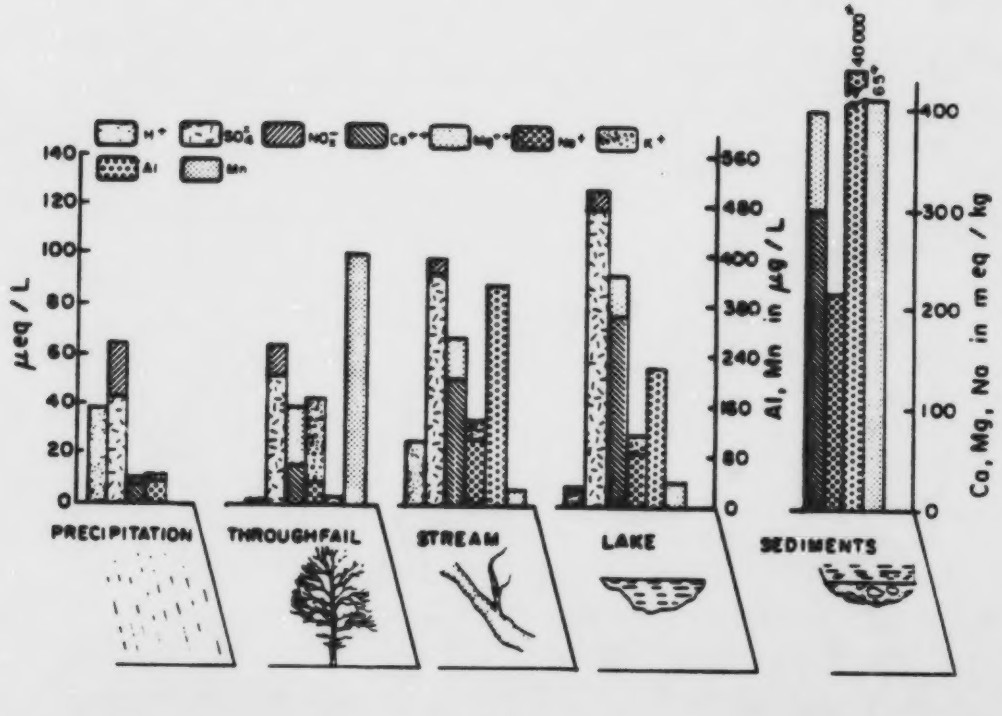

Figure 15. Schematic representation of the chemical composition of the water as it flows through the various hydrological compartments of the Tantaré watershed (* in ppm).

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DISCUSSION

Question:	In our trace element deposition studies at Hubbard Brook in New Hampshire we have detected a dramatic decrease in lead input in precipitation since 1978. Is there any similar evidence in Québec?
Answer:	No, we have not yet observed such a decrease. In order to evaluate the impact of using more unleaded gasoline by the auto transport industry we have stratigraphically sampled the sediments of a small headwater lake in the Laurentide Park which is heavily contaminated by road salts (conductivity 350 μmho cm^{-1}). The geochemical results will be available in a few months.
Question:	Could you comment on your 1940 data presented on NO_x and SO_x values and pH that you showed? What is the accuracy?
Answer:	The data for 1940 were obtained from an EPA report dated 1978. Similar values do not exist for Canada. These early emission data are considered to be ±50% accurate, but the ones from 1965 onward are much more reliable. I have hypothesized a natural pH of 5.6 before 1940 because sediment cores ($\approx$30) throughout the province showed an unpolluted natural lead level lower than 2 ppm and I assumed from this that anthropogenic acidification was not a problem in Québec before 1940.

Question: **What is the relative contribution from surface runoff for lead accumulation in the lake?**

Answer: **Unlike the Zn inputs coming from the watershed it is difficult for me to tell. The late Professor Rigler and students at McGill University tended to believe that it is negligible. I do not see why some of it should not be passing from the watershed to the lake sediments under the particulate phase just like ^{137}Cs is doing. We know that Pb is mobilized only at fairly low pH.**

Acid Stress on Forest Habitats: Implications for Terrestrial Wildlife

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ABSTRACT

Forests and their stratified structure provide a diversity of habitats for a variety of wildlife species. Although the influence of acidic deposition on forests is incompletely known, preliminary research indicates impacts may occur. Because of these impacts and the potential for subsequent change in forest structure and function, there is a suspected impact on the wildlife inhabitants. In most cases, these impacts are not direct, but instead arise from modification of the habitat and changes in trophic relationships. Such changes, which are often subtle, challenge methods of measurement. Detection of changes distinguishable from normal spatio-temporal variations in wildlife populations is difficult. The net result over time, however, may be significant enough for concern. This paper provides an overview of the current information on the impacts of acidic deposition and its precursors on forest resources and the possible implications for terrestrial wildlife.

INTRODUCTION

In the invitation to this conference, Dr. Rennie asked that we provide an overview on the topic "Terrestrial Wildlife" in relation to acid rain and forest resources. Much of what is discussed in this paper comes from four recent reports which have compiled most of the available information on acid precipitation impacts on terrestrial wildlife. These reports are the Memorandum of Intent (MOI 1983) document, the Critical Assessment documents (Altshuller and Linthurst 1983), the Canadian Wildlife Service (CWS) report (Clark and Fischer 1981) and the U.S. Fish and Wildlife Service (FWS) series of reports (Peterson 1982; Borghi 1982; Newman 1980). We have freely taken information from these publications and acknowledge their major contribution to this discussion.

A cursory review of the major ecosystem-level studies involving acid precipitation quickly establishes the fact that the primary research emphasis has been on forest and aquatic systems (Table 1). Within these programs, there are only a relatively few studies investigating effects on wildlife. Likewise, a recent inventory of research on acid deposition and forest effects, supported by the private sector in the U.S., showed no specific research directed toward terrestrial wildlife (General Research Corporation 1983). In Scandinavia, where much of the initial acid rain research was conducted, projects have also shown a general lack of effort concerned with investigating effects on terrestrial wildlife. In Poland and Czechoslovakia, there are several field programs focused on the effects of industrial air emissions on forests and wildlife, and although these projects do not deal with acid precipitation specifically, the findings represent useful examples of direct and indirect effects of airborne pollutants on terrestrial species (e.g., Newman 1980).

Although there are a number of projects in the U.S. National Acid Precipitation Assessment Program (NAPAP) that are developing information on forest ecosystem response to acidic deposition, again there are few projects that deal specifically with wildlife. The exceptions are the studies being conducted on amphibians and waterfowl, and the reports summarizing the literature on the effects on fish and wildlife (ITFAP 1982, 1983).

In Canada, the 1983 Environment Canada catalogue of research on long-range transport of air pollutants and acidic precipitation lists about six projects on wildlife, primarily aquatic birds (Environment Canada 1983).

Even though the research and public interest concerning the effects of acid rain on wildlife resources have increased in the past few years, our understanding of the mechanisms for cause and effect and our estimate of its magnitude still remain very uncertain. There are several reasons for this. The assessment of the problem is complicated by the fact that acid precipitation represents another incremental impact that must be weighed against a multitude of subacute environmental stresses to which wildlife populations are exposed. Our ability to detect or segregate the specific impact or effect of acid precipitation from the host of factors that bear on the homeostasis of individuals or populations is limited. As tools and technology are developed to improve these measurements, our understanding increases, but the costs associated with the multidisciplinary research required to follow changes in productivity and trophic structure which affect wildlife are high.

It is evident that the paucity of data prevents the compilation of a list of definitive and conclusive statements on the impact of acid precipitation on forest wildlife. Therefore, in this overview, we shall examine some of the potential pathways for effects and, where possible, provide examples of the research on acidic deposition and forest ecosystems, and the likely mechanisms whereby wildlife could be affected.

HISTORICAL EVIDENCE

To begin this overview, it may be helpful to develop some historical perspective of the problem. There are essentially three categories of air pollutants: (1) Photochemical oxidants; (2) Particulates; (3) Acidifying air pollutants (Peterson 1982). Although this conference is specifically addressing "acidifying pollutants," it is important to recognize these other categories as part of the atmospheric composition that bathes the forest ecosystem and contributes to the total effect on its structure and function. This is mentioned also because much of the information on effects on terrestrial wildlife comes in part from studies of this broader group of airborne pollutants. A number of the materials considered atmospheric pollutants (e.g., zinc) are essential to animals and plants in trace quantities. The margin between a beneficial or necessary amount and a toxic amount of the element may be small. Below the required amount, deficiency conditions occur, and above, the organism is responding to a toxic chemical.

There have been over 100 reported air pollution episodes involving injury or death to animals since the end of the 19th century (Newman 1980). These incidents tend to be extreme cases where there were chronic levels of exposure to gaseous pollutants or toxic materials. Some of the incidents involving the adverse effects of these airborne pollutants on mammals and birds are summarized in Table 2. In the cases reported, the mammals are primarily herbivores. This may be mainly the result of the ingestion of heavily contaminated vegetation near the pollution source. The earliest incident, involving arsenic poisoning of fallow deer (*Dama dama*) in Germany, was recorded in 1887. For birds, there are examples of granivores, insectivores and carnivores being affected in various ways by air emissions. This table provides evidence of the pathways by which these contaminants affect wildlife and some of the responses elicited by specific pollutants. These responses can be generally categorized as either physiological (Table 3) or ecological (Table 4). It is evident that the effects may range between quite subtle, such as a change in population numbers, to dramatic, such as a death of individual animals. In some cases, the response may even be specific enough that the species can be used as a biological indicator of a particular pollutant (Newman 1980).

Table 1. Major ecosystem studies on the effects of air emissions in North America

Name of Study	Ecosystem (Location)	Pollutant Stress
Experimental Lakes Area (ELA) Watershed Studies	Northern coniferous forest (Ontario)	Acid deposition
Turkey Lake Forest Watershed Study	Northern deciduous forest (Ontario)	Acid deposition
Dorset Watershed Studies	Northern forest (Ontario)	Acid deposition
Montmorency Experimental Forest Study	Northern coniferous forest & associated lakes (Quebec)	Acid deposition
Kejimkujik Calibrated Catchment Program	Maritime coniferous forest (Nova Scotia)	Acid deposition
Kaybob Gas Plant Study	Transition montane boreal forest (Alberta)	SO_2
San Bernardino Mtn. Study	Mixed coniferous forest (California)	Oxidants
Hubbard Brook Ecosystem Project	Northern mixed deciduous coniferous forest (New Hampshire)	Atmospheric deposition including acid and trace elements
Walker Branch Watershed Study	Mixed deciduous forest (Tennessee)	Atmospheric deposition, including acid and trace elements
Whitecourt Gas Plant Study	Mixed coniferous forest (Alberta)	SO_2
Integrated Lake-Watershed Acidification Study (ILWAS)	Northeastern deciduous forest (New York)	Acid deposition

From Newman and Schreiber, in press.

CURRENT INFORMATION ON EFFECTS ON FOREST WILDLIFE

At present, our best information base for effects on animals from acid precipitation is in the aquatic environment, where surface water acidification and resulting impacts on aquatic biota have been demonstrated. As the effects on fish have been widely documented (e.g., Beamish 1974; Haines 1981), it is reasonable to assume that there will also be effects upon those terrestrial species of wildlife that are associated with or directly dependent on the aquatic environment at some stage in their life cycle.

Ponds and temporary meltwater pools, which commonly form in forests in early spring, provide important breeding habitats for a number of amphibian species. In the U.S., it is estimated that about 50% of the species of frogs and toads and about 30% of the salamanders use ephemeral forest ponds for reproduction (Pough and Wilson 1977). These small pools and ponds are likely to be acidic since they receive snowmelt and spring rains which have little contact with the soil buffering system. Studies have shown a number of amphibian species are susceptible to the effects of pH depression (Table 5). Low pH reduces the reproductive capability of amphibians in a number of ways (Table 6). The long-term effect could well be changes in populations, distribution, and species diversity. In the Hubbard Brook Experimental Forest of New Hampshire, salamanders disappeared from the study area when a section of Hubbard Brook was artificially acidified to a mean pH of 4.0 (Hall and Likens 1980). Other examples of how amphibian populations are affected include the natterjack toad (***Bufo calamita***), which was not found in ponds below pH 5.0 (Beebee and Griffin 1977), and the smooth newt (***Titurus vulgaris***), which was rarely found in ponds below pH 6.0 (Cooke and Frazer 1976). In Sweden, Hagstrom (1977) observed that the common toad (***Bufo bufo***) and common frog (***Rana temporia***) disappeared when the pH levels fell below 4.0-4.5. In terms of the forest ecosystem, such changes could lead to a number of ramifications. Amphibians are important predators of herbivores in these aquatic systems, and alterations in their abundance or diversity could have an effect on both higher and lower trophic levels. Amphibians, specifically salamanders, represent a significant component of the biomass in the forest (Burton and Likens 1975). They are primary energy movers in the ecosystem and provide a high-quality food resource for a variety of vertebrate predators, including snakes, birds and mammals. A reduction in amphibian populations would presumably affect such tertiary consumers and the subsequent cycling of nutrients.

Loss of fish and other aquatic biota from acidified lakes, ponds and wetlands may well cause certain shifts in the predator-prey relations of a number of wildlife species. Clark and Fischer (1981) in their CWS report used these associations to develop a number of tables relating wildlife species and the potential effects of acid deposition through their food resources. These lists focus on wildlife species with ranges overlapping areas of known acid deposition. Their diets are composed in part of aquatic organisms whose populations may be reduced by the effects of acid precipitation (Tables 7, 8, and 9). A cautionary note should be added that these are proposed impacts for the most part and there has been little research actually conducted on the effects on the species or on their food webs.

Waterfowl or, more generally, water birds are another group of animals that utilize both aquatic and terrestrial habitats and may exhibit effects from acid precipitation (Table 10). Acidification of forest ponds and lakes affects the availability of organisms which serve as food resources for wildlife and habitat used for cover and nesting sites. Current studies by the U.S. Fish and Wildlife Service and the Canadian Wildlife Service are investigating these potential impacts. Preliminary results from these studies indicate that some headwater ponds and wetland areas important for breeding are vulnerable to acidification (McNicol and Ross 1982). Lake acidity may be a factor in determining water bird habitat quality and the selection of nesting sites by the different species. The black duck (***Anas rubripes***) and common loon (***Gavia immer***), for example, were found to avoid acid lakes in southern Quebec (Desgranges and Darveau, in prep.). Research is continuing in both the U.S. and Canada on the effect of acidification on waterfowl productivity due to changes in water chemistry and the availability of food resources.

Table 2 Examples of incidents involving the adverse effects of airborne pollutants on wildlife

Pollutant	Species	Effects	Location	Reference
General air pollution	Larks	Reduced populations	Japan	Miyamoto 1975
SO_2, particulates, NO_x, fluoride	House martins	Reduced nesting	Czechoslovakia	Newman and Novakova 1979
SO_2, particulates	Roe deer	Reduced antler quality	Poland	Jop 1979
SO_2, fly ash	Hares	Hypocalcemia & hypoproteinesis	Czechoslovakia	Novakova & Roubal 1971; Novakova et al. 1973
Particulates	House martins, swifts	Reduced populations	England	Cramp & Gooders 1967; Gooders 1968
Fluoride	White-tailed deer	Fluorosis	Canada	Karstad 1967
	Black-tailed deer	Browse contamination	U.S.A.	Newman & Murphy 1979
	Field mice, voles	Biological concentrations	England	Wright et al. 1978
	House sparrows	Biological concentrations	Czechoslovakia	Balazova & Illuchan 1969
Hydrogen sulfide	Passerine birds	Death of hundreds of birds	Canada	Harris 1971
			U.S.A.	Yont & Sayers 1927
Oxidants	Small mammals	Reduced populations	U.S.A.	Kolb & White 1975
	Deer mice	Genetic change in sensitivity to ozone	U.S.A.	Kirhkind 1979
	House sparrows	Respiratory lesions	U.S.A.	Wellings 1970
Arsenic	Fallow deer	Death	Germany	Tendron 1964
	Red & roe deer, rabbits			Prell 1936
Lead, cadmium, copper	Voles, mice & shrews	Biological concentrations	U.S.A.	Hirao & Patterson 1974; Schlesinger & Potter 1974
Cadmium	Sparrow	Death of birds	Japan	Nishino et al. 1973
	Sparrowhawks, song thrushes	Food chain magnification	England	Martin & Coughtrey 1975, 1976
Mercury	Wood mice, bank voles	Biological concentrations	England	Bull et al. 1977

Table 3. Responses of wildlife to air emissions

Physiological Responses
Changes in blood chemistry or physiology
Changes in cellular enzymes
Changes in energy requirements for normal activities
Change in growth rates
Change in genetic resistance
Lowered resistance to natural environmental stress
Residue accumulation
Teratogenic, mutagenic or carcinogenic effects

From Newman 1975.

Table 4. Responses of wildlife to air emissions

Ecological Responses
Change in population numbers
Change in spatial distribution
Change in appearance
Change in birth rate
Change in death rate
Abnormal behavior

From Newman 1975.

Table 5. Susceptibility of Breeding Habitat to pH Depression for Those Amphibians in Northeastern North America Whose Range Overlaps Areas Receiving Acidic Deposition

Potential for Acidification of Egg-laying Habitat	Habitat	Common Name
High	Meltwater Pools	Yellow-spotted Salamander Blue-spotted Salamander Tremblays Salamander American Toad Chorus Frog Wood Frog Northern Leopard Frog Northern Spring Peeper Gray Tree Frog
Moderate	Permanent Ponds	Mudpuppy Red-Spotted Newt American Toad Gray Tree Frog Chorus Frog Bullfrog Green Frog Northern Leopard Frog Mink Frog
	Streams	Northern Two-lined Salamander Mudpuppy
	Lakes	Bullfrog
Low	Bogs	Four-toed Salamander
	Logs & Stumps	Red-backed Salamander

Modified from Clark and Fischer 1981.

Table 6. Reported Effects on Amphibians from pH Depression

Embryonic mortalities and deformities
Decreased egg masses
Reduced densities
Increased percentage of dead or moulded egg masses
Iono-regulatory failure
Delayed development
Abnormalities
Decreased sperm motility

From MOI, 1983.

Table 7. The Food Resources of Snake Species That May Be Reduced Due to Acid Precipitation

Potential Effect on Food Resources	Habitat	Species
Reduced biomass of fish, amphibians, aquatic invertebrates	Wetlands	Northern Water Snake
Reduced biomass of earthworms, amphibians, minnows		Eastern Garter Snake
Reduced biomass of amphibians, minnows		Eastern Fox Snake
Reduced biomass of amphibians	Meadows & woodlands	Eastern Hognose Snake Eastern Milk Snake Eastern Mississauga Rattler
Reduced biomass of aquatic invertebrates and amphibians		Northern Ring-necked Snake

Modified from Clark and Fischer 1981.

Table 8. The Habitat and Diet of Turtle Species Whose Range Extends into Acid Precipitation Impacted Areas in Canada

Habitat	Diet	Species
Lakes, Ponds	Aquatic Invertebrates	Midland Painted Turtle
	Amphibians, fish	Blandings Turtle
	Aquatic plants, invertebrates	Snapping Turtle
Woodlands	Aquatic invertebrates, amphibians, fruits and berries	Wood Turtle

From Clark and Fischer 1981.

Table 9. Mammalian Species With Diets Largely Composed of Organisms Whose Biomass May Be Reduced Due to Acid Precipitation

Potential Effect on Food Resources	Habitat	Species
Reduced biomass of amphibians, aquatic invertebrates, fish	Wetlands	American Mink River Otter
Reduced biomass of aquatic invertebrates	Wetlands	American Water Shrew
Reduced biomass of terrestrial invertebrates	Wetlands	Common Shrew Arctic Shrew

Modified from Clark and Fischer 1981.

Table 10. Avian Species Most Likely to Be Influenced by a Reduction in Food Resources Due to Acid Precipitation

Potential Effect	Feeding Habitat	Species
Reduced biomass of fish, aquatic invertebrates, amphibians	Lakes	Common Loon Osprey
	Littoral zone	Great Blue Heron American Bittern Belted Kingfisher Hooded Merganser Common Merganser
Reduced biomass of aquatic invertebrates	Littoral zone	Common Goldeneye Red-breasted Merganser Ring-necked Duck Black Duck Virginia Rail
	Riparian	Spotted Sandpiper
Reduced biomass of aquatic invertebrates with adult stage terrestrial invertebrates	Wetlands	Eastern Kingbird Eastern Phoebe Tree Swallow Barn Swallow Bank Swallow Myrtle Warbler Blackpoll Warbler Palm Warbler Common Yellowthroat

Modified from Clark and Fischer 1981.

Forests provide a wide diversity of habitats and food resources for animals. It follows that any damage from acid precipitation to forest ecosystems has the potential to interfere with the trophic relationships established between forest vegetation and the animal communities. The detection and understanding of these effects are complicated by lack of understanding concerning the resilience of forest ecosystems, and the compensatory mechanisms of individual species and populations of wildlife. It is presumed that for species of terrestrial wildlife, the impacts from acidification are most likely to be expressed in response to the changes produced through the soils and vegetation. For example, studies in the San Bernardino Forest of California suggest the abundance and distribution of small mammals has been changed by the effects of air pollution on the quality of key vegetation and soil habitat requirements (Miller and Elderman 1977). As shown by other papers at this conference, acid deposition can influence forest soils and vegetation in a variety of ways. The impact and the interpretation of a change in either habitat or food resources will depend in part on the availability of suitable alternative habitat or food sources. Species with very narrow habitat requirements or very selective diets (stenophagic) will be most at risk.

In the broad sense, terrestrial wildlife includes the invertebrates and microorganisms of the forest. Reviews such as the Critical Assessment Document (Altshuller and Linthurst 1983) and others (e.g., Drablos and Tollan 1980 MOI 1983;) provide details on these species so they are not included in this overview. It is important to note, however, that microbial activity is inhibited at low pH. This decline results in reduced decomposition of organic material and an inhibition of nutrient cycling (Almer et al. 1974). The activities of these organisms are part of highly important biological processes which form the base of the ecosystem support that is initially impacted, and which triggers further responses at higher trophic levels. Soil animals, such as earthworms and millipedes for example, can exhibit reduced populations in acid soils. Species such as these are highly significant in the energy and nutrient cycling of the forests and are major prey items for a variety of vertebrate species. Likewise, forest insects are important in the vertebrate food chain and may be impacted by acid deposition. These interactions are not well enough understood to permit assessment at this time.

Degradation of forest habitat from acid deposition can occur in a number of ways, including foliar injury, loss of sensitive plant species and loss of productivity. Generally, the diversity of animal life is associated with the stratification and growth forms of the plants. Any structural simplification of forest ecosystems that reduces the number of niches will have a probable effect on wildlife. Damage to vegetation may interfere with the specific ecological requirement of a species. An example of this may be the northern parula (*Parula americana*), which requires certain types of lichens for nesting material. *Usnea* species are extremely sensitive to air pollution, and the reduction of this lichen group in eastern North America appears related to acid precipitation (Arbib 1980). The parula's distribution has subsequently become reduced with the reduction of the lichen, and it has been proposed that acid precipitation has been a contributing factor (Arbib 1980).

Forest die-back has been linked to acid precipitation in Europe and North America, affecting spruce, maple, beech and oak (e.g., Ulrich 1982; Vogelmann 1982). These tree species have an important value to wildlife (Martin et al. 1951), and a reduction in their abundance could influence the presence of a number of wildlife species. Oaks are particularly important to wildlife, providing a staple in the diet of many species and a source of cover and nesting material for many species of birds and mammals. Until the effects on such tree species are more established, however, consequences to wildlife are speculative.

There is some evidence that the photosynthetic efficiency and nutritional value of vegetation may be influenced by acid deposition (Lechowicz 1981; Shaw 1981; Grodzinska 1977). The quality of browse is one expression of the result of nutrient cycling and metal contamination that would be reflected in the consumer population. An example of this is the interaction between sulfate and selenium in browse species of herbivores (Shaw and Cocks 1982; Shaw 1983). From studies on domestic livestock and their forages, the link between increased sulfate fertilization and soil-plant systems, such as might occur with acid deposition, has been found to interfere with the availability and uptake of essential trace elements (Allaway 1970). It has been demonstrated that excessive sulfur in a plant community can inhibit the transfer and function of selenium in the soil-plant-animal food chain (Davies and Watkinson 1966; Gissel-Nielsen 1973; Shaw 1981). Excess sulfate in the diet of herbivores may induce excretion of selenium which is important in enzymatic and other metabolic functions of the animal (Harr 1978). Symptoms of selenium deficiency documented for domestic herbivores include white muscle disease and reproductive failure, including abortion, infertility and neonatal mortality (Schwarz and Foltz 1957; Oldfield 1972). Tests of this phenomenon in wild animals are incomplete, although several cases for wild herbivores have been reported (Herbert and Cowan 1971.

Another indirect effect of the acidification of soils and water bodies is the potential for increased bioavailability of toxic metals to wildlife. Elevated levels of metals such as mercury, cadmium and lead have been found in lake waters and in the biota from acidified areas of North America (Schofield 1976; Scheider et al. 1979; Suns et al. 1980). In regions remote from direct sources of contamination, higher levels of metals are being found in tissues of wildlife associated with acid-stressed, as compared with non-acid stressed, habitats. For example, eggs of the common goldeneye (*Bucephala clangula*) collected from an acidified region of Sweden were found to have high mercury concentrations as compared to nearby buffered lakes (Eriksson et al. 1980), and raccoons (*Procyon lotor*) from the Muskoka area of Ontario were found to have liver-mercury levels five times greater than those from a non- acidified area of the province (Wren et al. 1980). As well, an analysis of cadmium in the tissues of moose (*Alces alces*) and roe deer (*Capreolus capreolus*) collected in Sweden in areas remote from direct industrial pollution has established an age-dependent increase in this metal for a sample of 38 moose and 56 roe deer (Frank et al. 1981; Mattsson et al. 1981). There is also evidence from Swedish studies of eggshell impairment in song birds that feed on aquatic invertebrates contaminated by aluminum mobilized under acid conditions during springmelt (Nyholm and Myhrberg 1977; Nyholm 1981). Another interesting example concerning habitat degradation and wildlife quality comes from Poland (Sawicka-Kapusta 1978, 1979, Jop 1979;). In this study, a population of roe deer from a pine forest impacted by sulfur dioxide and particulate emissions was studied. The research showed a significant decline in the length, volume, weight and trophy value of the antlers that coincided with exposure to the airborne pollutants (Fig. 1). In view of these observations, the question of accumulation and movement of toxic metals through the food chain, as affected by pH changes, needs further investigation.

These few examples indicate there can be a number of impacts on wildlife from air pollutants, including acid deposition. Unfortunately, the data base is very restricted, and most conclusions must be considered tentative.

SUMMARY

In this brief overview, we have indicated some of the concerns for terrestrial wildlife and the impacts of acidic deposition. Effects have been postulated and are being tested within the current capabilities of science. It remains the charge of the scientific community to develop the right hypotheses for testing, establishing the band of uncertainty associated with a given proposition, and then implementing the research that is required to limit the uncertainty to acceptable limits or provide information that is able to resolve the issue (IERE 1981). Those words came from another conference that addressed the ecological problems of air pollution, and they are still appropriate. With completion of some of the current wildlife research, and as new information is developed by forest ecologists, we will be better able to answer some of these questions. Because most of the pathways between the forest plant community and animal community are interactive, exchange of information should be mutually beneficial to both forest and wildlife scientists.

Brungs (1980) has likened an environmental impact, such as acid rain, to a sometimes selective, sometimes non-selective predator. In the unaffected ecosystem, species diversity is directly related to the efficiency by which predators prevent monopolization by one or a few species. Some level of predation is acceptable since it may reduce the density of a dominant species and promote diversity. However, if the predation, or impact of acid rain in this case, becomes excessive, the resilience of the population is threatened. The less successful or less tolerant species are reduced or eliminated, and the direction is narrowed toward monocultures, less diversity and, in accordance with general ecological principles, a less desirable ecosystem.

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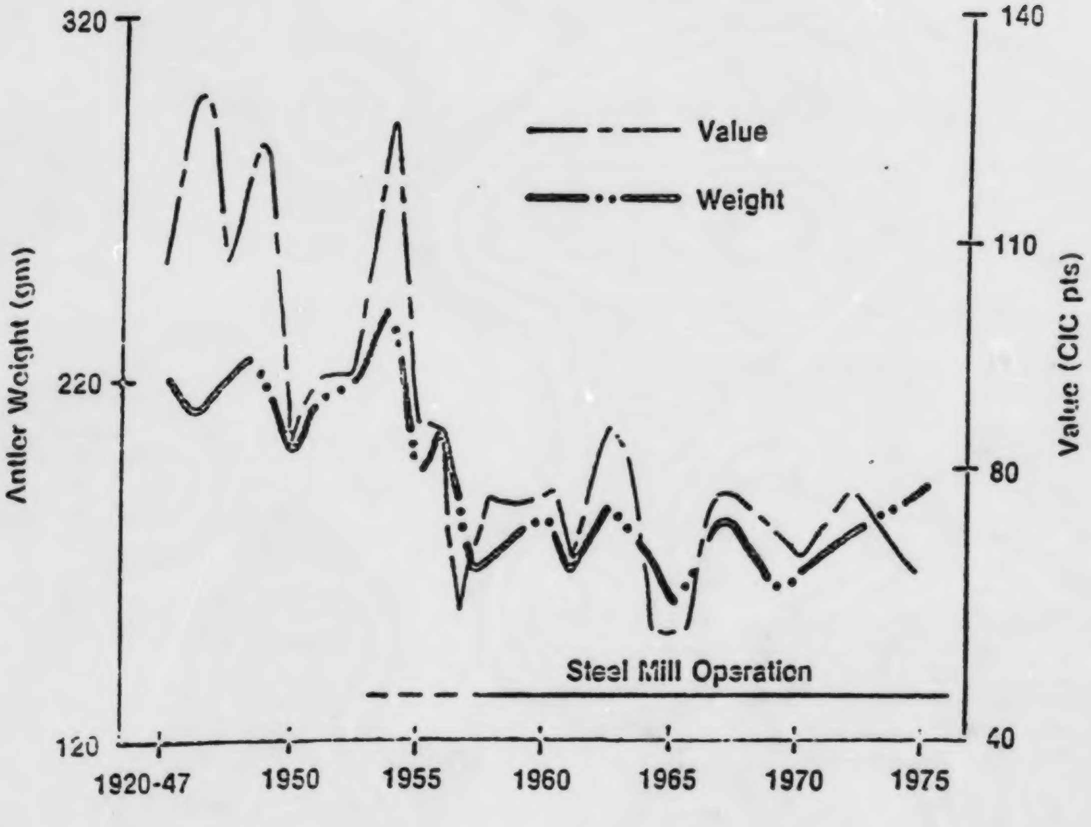

Figure 1. Change in roe deer antler weight and value in Niepolomice Forest, Poland (adapted from Jop 1979; taken from Newman 1980).

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DISCUSSION

Question: Could you comment on the use of behavioral abnormalities to detect toxic effects on terrestrial wildlife?

Answer: Yes, that is a method to determine toxicity effects. We can include things like lameness, abnormal movement and so on. The symptoms for lead poisoning include bellowing, roaring, staggering about with rolling eyes, frothing at the mouth, excitement and delerium.

TECHNICAL SESSION VII
IMPLICATIONS OF ACID RAIN FOR FOREST ECOSYSTEMS

Resource Sensitivity Assessment

William W. McFee

INTRODUCTION

When we feel threatened or under attack, one of our first reactions is to assess our vulnerability. Where are we most likely to be injured or damaged? It is a natural reaction.

At the threat of resource injury to soils, vegetation, and waters by the atmospheric deposition of acidic substances, many scientists begin to seek ways to estimate the extent of resources at risk. Where are the lakes and streams, soils, or vegetation types most likely to be damaged? What is their extent?

I shall describe the nature of these assessments or attempts at mapping, give several examples, and finish by commenting on their usefulness.

What are these sensitivity assessments? They are all attempts to describe the resources at risk and to portray the locations where they are most vulnerable. All assessments attempt to use current knowledge and available data to predict effects. They are efforts to use the present data without collecting a lot of new field data. All of them generalize spatially, and this depends upon the scale. Some of them are very broad-brush treatments, others get into some detail, at least down to a county level. All of them are based on assumptions about reactions that go on in nature and on the relations of these reactions to properties of the system and acidic impacts on which there are data. I am going to discuss these efforts critically because several have given erroneous impressions on actual damage when in certain cases it has not yet been demonstrated.

A DISCUSSION OF EXISTING ASSESSMENTS

One of the first attempts at resource assessment sensitivity to acid precipitation in North America was published by Galloway and Cowling in 1978. Using a generalized bedrock map coupled with some alkalinity data, they produced a very generalized map of the areas where surface waters were most likely to be affected by acid deposition. One of the problems I will discuss is already apparent with this kind of map. Areas on the map are simply labelled "sensitive" areas. One can ask "sensitive to what"? Does that mean that the forests in those regions are going to decline, that the soils are going to become more acid, that the lakes are going to lose all their fish? When these authors prepared the map they meant it to refer to areas where lakes were likely to be found sensitive to acidification. They did not intend a more comprehensive extrapolation.

Another broad-brush treatment was done by Nieman et al. in 1979 for EPA. They attempted to integrate geology, soil, climate, and vegetation information in a qualitative way to produce a U.S. map of so-called "sensitive areas", and this is probably one of the most limited because criteria of sensitivity were not defined, so the interpretation is obscure. Unfortunately, there is a tendency to deduce a whole lot of things that have little basis in fact. The map is not specific at all about the damage that is likely or what sensitivity means.

At a meeting in Gatlinburg in 1979 on atmospheric deposition of sulfur, three papers were given on regional assessments. One by Kopatek, Harris, and Olsen on regional assessment of soil sensitivity was done in quite a reasonable fashion. These authors used computer data-base information for the typical soils of a county and the available Soil Conservation Service data on cation exchange, base saturation, pH, base content, etc. to estimate the sensitivity of those soils to acidification. In other words, the soils with low cation exchange capacity and a high or slightly acid pH were the ones most likely to be acidified. At that same meeting, I presented a paper and some maps purporting to show the sensitivity of soil regions to long-term acid precipitation. I was attempting to estimate sensitivity to acidification and release of aluminum and other toxic ions harmful to aquatic systems. I did this based on cation exchange capacity and on the presence or absence of carbonates in the soil and the presence or absence of renewal by flooding.

Starting with soil association maps of individual states and the data that were available for these I interpreted soil association maps for key characteristics, principally cation exchange capacity, and produced maps that were rated sensitive, slightly sensitive, non sensitive, and so forth. Orange denoted the most sensitive, yellow the next most sensitive, and green the least or non-sensitive. I had good soil association maps in some states, but very poor ones in others.

In retrospect, I think it was a mistake trying to develop maps that did two things at once. The assumption was, of course, that if the soil had high cation exchange capacity, it was likely to have a high base status (which is not necessarily so) and, therefore, be resistant to the effects of acid rain either in moving acid through it or by acidifying the soil. The other end of the spectrum was less debatable: if the soil had a low cation exchange capacity, then it certainly had to have a low resistance to the effects of acid rain in moving materials through it.

Following this same line of reasoning, other attempts have been made: one in western Canada by Holowaychuk and Lindsay. They developed a sensitivity system very similar to the one that I used and very similar to the ones that have been used by some others. They ranked the soils according to their buffering capacity. The most sensitive were those with low buffering capacity and only slightly acid. The assumption was that these soils would be the ones likely to change most rapidly in pH. A map was produced of the Sand River area in Alberta in which pink delineated the most sensitive area, green the least sensitive, and blue intermediate in sensitivity, based primarily upon cation exchange capacity and the degree of base saturation or on the total exchangeable basis.

In 1981, Wang and Coote in Canada developed a sensitivity classification of agricultural land to long-term acid precipitation following some of the same lines of thought. Anything that had surface soil exchange capacities, that is the exchange capacity times its percent base saturation, of less than 6 meq 100 g^{-1} was considered sensitive. This is based on the same sort of reasoning and assumptions that Holowaychuk, Lindsay, and I used and means that for a soil with less than 6 meq 100 g^{-1} it would be possible to remove 25% of the bases of the upper 15 cm in 25 years if it were receiving 1.2 keq ha^{-1} yr^{-1} of acid. Well, that is probably about the largest amount of acid being received anywhere in northeastern U.S. It is certainly more than is being received in wet deposition, which is fairly well known, and it is a fair estimate of what we are getting in both wet plus dry forms. But, of course, there are a lot of assumptions involved. In a worst case scenario it assumes that nothing else is happening in the soil except the removal of these bases by the incoming acid. Wang and Coote were, of course, mapping the agricultural soils of eastern Canada. Their approach seems reasonable, and their maps provide a fair estimate of those soils with the greatest potential to acidify. The danger implicit in the maps is that they suggest agricultural soils are at risk anytime they are mapped and labelled sensitive or non-sensitive. In fact, no soil scientists working in agriculture would agree with this suggestion because almost all agricultural soils receive some lime fertilizer or other cultural treatments that would vastly overshadow any effects of acid deposition.

Turning now to a few of the efforts in the aquatic side — just as illustrations of other ways of approaching sensitivity mapping — reference may be made to another paper presented at the same Gatlinburg meeting in 1979 by Steve Norton. He was attempting to refine and do the same sorts of things that Galloway and Cowling had done earlier, and he defined four bedrock types according to their ability to buffer acid precipitation and therefore their ability to neutralize effects on the aquatic system. Class one type had essentially no or very low buffering capacity and included bedrocks made up of granites, quartz, sandstone, etc. There were then a medium to low buffering capacity then a high to medium class and finally one containing carbonates and limestone that would have almost an infinite buffering capacity. He then mapped the percentages of these by county and used these percentages to rank counties as to sensitivity. The same approach was developed further at Brookhaven National Laboratory from which it could be shown that the dominance of a particular soil Order, such as Alfisols, could refine bedrock mapping toward a better prediction of surface water alkalinity.

And then going back to what Norton had done in a publication by Hendrey and Norton and others, they extended Norton's system to the whole eastern United States. A later NADP publication, as an atlas, extended it to all the lower 48 states. Maps are available showing Norton's system applied county by county to the eastern United States. Types 1 and 2 soils or bedrock are shown red; these have very low buffering capacity. Areas that have no bedrock of Type 1 or 2 are shown yellow, and the blue is used for Type 2 only. In other words, red areas are most likely to have aquatic systems sensitive to acidification. Unfortunately, this map has been issued as showing the "sensitivity of ecosystems as determined by bedrock". This is a misuse of what Norton had intended; when he developed the original map he meant to say the "sensitivity of aquatic systems to acidification as determined by bedrock".

Going back now to forest systems, in 1980 Robitaille produced a paper on acid precipitation and vegetation. He used the relative species abundance and the sensitivity of those species to sulphur dioxide to rank the sensitivity of vegetation regions in Canada. Unfortunately, this map was labelled "acid precipitation and vegetation" because at the time the only data available on sensitivity of vegetation were essentially sensitivity to SO_2 and not to the wet deposition of acid rain. These examples show the dangers associated with this kind of approach when pioneering studies are interpreted far beyond their original constraints. Not always are the limitations understood, so that generalizations are passed on to become unquestionable facts.

Another approach was by Coker and Shiltz. They developed a system of classifying geologic materials — on this occasion not just the bedrock, but also the glacial deposits, the composition of which they used, along with that of lake sediments, as an indication of where existed the greatest potential for acidification and the release of noxious substances. This has been subsequently refined but at the time was going somewhat further than Hendrey and Norton's work in the U.S.

Cowell, Lucas, and Rubic developed an ecological sensitivity rating for acid precipitation. What they were attempting to do was to integrate all of the known factors that might influence an ecosystem's sensitivity to the input of acidic materials. But what they found available was much more limited than what they would like to have had, and they ended up using "petrography", which is really some soil characteristics, primarily texture, and soil depth and bedrock to produce an ecodistrict sensitivity map. Again, I think the publication of such a map implies a lot more than it can possibly do. Once published, it says that we know which ecosystems are most likely to be sensitive to acid deposition, when, in fact, we do not know for sure that any of them are really sensitive or are going to show any change.

One of the arguments that I should like to conclude with is that we should limit our mapping to single characteristics or at least to very limited sets of characteristics, for which we have firm data. We should not apply labels that imply a knowledge that we do not have, or that require an understanding of reactions that is beyond current limitations.

I should like to cite an example from the aquatic system again. A map was prepared of lake and stream water alkalinity for New York State. It was not labelled "sensitivity", but merely shows the level of water alkalinity. Omernick is doing this currently at the Corvallis EPA laboratory and has developed a map for the entire northeastern United States. The darkest areas on the map are the aquatic systems with surface waters, both streams and lakes, with the lowest alkalinity, and as the color gets lighter so the waters increase in alkalinity to over 400 μeq L^{-1}. The darkest is less than

50 μeq L^{-1}. He has extended this mapping to the entire United States on a small-scale map without dividing up the alkalinity classes so finely.

I was curious as to how they drew the lines when I knew all they had available were rather isolated points for known alkalinities for streams and lakes. In discussions with them I found that they overlaid their map of alkalinity data with maps of several natural features, geology, soils, land use, etc. to see if they made any sort of reasonable correlation. They found that the land-use maps were the most useful, but also the geologic and soils maps helped them decide the directions to draw the lines. In many cases they found the alkalinity groupings corresponded quite well with the land-use maps. So even in this case where they were simply mapping a single characteristic, there is some interpretation and some generalization, especially spatial generalization, that may lead to false impressions.

SUMMARY AND CONCLUSIONS

Now I want to go back to acknowledge or point out that Cowell and Lucas, who have a poster at this meeting, have taken a reasonable approach to this matter of mapping resources. I encourage those of you that have not looked at the posters to go and look at their poster. They have a large map of eastern Canada which divides the terrain into 62 terrain classes based on the lithology, the soil texture and depth, and then they have a table that accompanies that map providing the interpretation. I think this is a very good approach because the basic map is a map of only terrain features which are not really changing; if the interpretation needs to be changed as to what is sensitive or insensitive, all that has to be done is to change the table which goes along with the map.

Also, an effort that I did not know enough about at the time I was preparing my talk is an effort by Olsen, Johnson, and Schriner at Oak Ridge National Laboratory. They have a publication which goes much further than their original one that I talked about by Klopatek, Harris, and Olsen. They are using a multi-stage approach, using counties as the mapping unit and producing maps of single important properties such as base saturation of the dominant soils, percentage of land in a certain land use, and the distribution of shallow or steep soils. They then add to that Hendrey and Norton's bedrock classification from their data base and produce a whole series of maps. They first map an individual characteristic and then combinations of them which permit further interpretations. Even this approach, which is one of the more advanced, is not without problems. One is that it uses counties as mapping units — in other words, the whole county has to show up as the same sort of uniform thing when in many cases there is tremendous variability within a county. Moreover, the soils data base is far from perfect; if the maps are examined, some things do not make sense in terms of what we know about the distribution of soils in the states. In many cases the data needed, such as sulphate absorption capacity, were just not available. Assumptions or estimates based on a best guess as to where sulphate absorption was the strongest had to be used. Everyone likes maps, but when we publish a map it is most likely to get a very wide usage; all the qualifications and explanations in our text may not accompany it.

I hope my colleagues who have done these assessments and mapping exercises will not think my paper is overly critical, but criticism can be applied to my own work as much as to anyone else's. What most of us have done is to imply a lot more than we say — in fact, we have implied a lot of knowledge that we do not have. We are guilty of suggesting a good understanding of deposition loading/ecosystem component interaction when that knowledge is not available. When we label a soil, lake, or vegetation sensitive or slightly sensitive, the implication to most people is that we know what will happen to those systems if exposed to acid rain. Sure, most of us deny this if you read everything that we wrote along with the maps we published. But the maps get used without all the accompanying qualifications from the text. For example, a map I prepared appeared with the caption "sensitive soils would lose more than 25% of their exchangeable cations after 25 years of 2 keq H^+ ha^{-1} yr^{-1}." In fact I did not say that. What I said was, "if all of the hydrogen replaced cations and there was no replacement (highly unlikely), then these sensitive soils *could* lose 25% of their basic cations in 25 years". Another example is the bedrock classification developed by Norton. His intention was that it would be used to predict the areas where surface water would be most likely affected by acid deposition. I have seen that map reprinted and called "a map of sensitive ecosystems in the eastern United States". But aside from the misuse of things we have prepared, we have been guilty of gross oversimplifications and implying a more complete understanding of these systems than we possess. I think that the efforts to combine several soil, geologic, vegetation, and water factors to produce a sensitivity map of ecodistricts or ecosystems require a lot more understanding. To do it implies a much more complete data base than we actually possess.

I think we should be very careful if we do any more of this mapping to clearly identify the resource or process at risk. For example, soil sensitivity is not adequate; we must say what kind of sensitivity we are talking about: to acidification, to the release of aluminum, or whatever. And furthermore, we should state sensitivity to what, to wet deposition of mineral acids, to the total potential acidic deposition, to SO_2 and NO_x concentrations in the atmosphere. In other words, we must be specific about the input.

I will finish by reminding all of us that the forest systems that we deal with are dynamic, complex, and defy complete characterization. We cannot expect all forests, not even all spruce forests on spodosols or podzols, to react the same way to needle exposure to acid rain or to the effects of 10-30 kg of sulphur and nitrogen deposited on the soil each year. Let us prepare our future assessments very deliberately and with clear definition of the risk and the resource at risk. While our relative rankings have some value, there is a great need for field verification before we go any further with these kinds of systems.

DISCUSSION

Question: Cation exchange capacity is measured at pH 7 by the Soil Conservation Service in the U.S. It can be very misleading for some typical spodosols (podzols). Could you comment?

Answer: The B horizons which have almost zero cation exchange capacity in the field may have very high cation exchange capacity when measured at pH 7 in a buffered solution. Since the cation-exchange capacity of these soils is almost entirely pH dependent, they may be 100% base saturated in the field. Hence there is a problem in using base saturation for predicting sensitivity. It is a serious problem. It would be important to have a data base that included cation exchange capacity.

Question: In most of the maps indicating sensitivities of forest or agricultural systems, cation exchange capacity or percent base saturation is used. No attention has been paid to differences that can be encountered in forest ecosystems compared to those in agriculture. Any comment?

Answer: My only comment would be that I work in an area where agriculture is very important, but I consider forest ecosystems to be much more at risk. My tendency is simply to ignore the agricultural system when we are talking about resources at risk. At least for now if we are going to have problems they are certainly going to crop up first in the aquatic system then in forest ecosystems not managed as intensively as agricultural systems.

Question: The U.S. Soil Conservation Service is conducting, at least in New York State, a new survey of soil characteristics and is surveying on a detailed county by county basis many areas of the U.S. Are they incorporating into their survey the sensitivity of our soils to acid deposition?

Answer: I cannot answer specifically what they are doing in New York, but I know what the service is doing in general and the answer would be no. They would not be making that kind of interpretation, but a lot of the field data that they are collecting will be useful for that purpose.

Question: I agree that single resources may better represent susceptibility to acidification. But to evaluate the global results it will be necessary to superimpose a number of these single resource maps. Do you think that this can bring erroneous interpretations because it may not take into account various interactions between different factors?

Answer: The answer is yes, because in many of the interpretations we are making assumptions which may be erroneous. The more of these we pile on each other, the more likely we are to come up with an erroneous conclusion. On the other hand, we cannot leave all of the interpretations to those who are less well informed.

Acidic Deposition and Air Pollution: Implications for Forest Management

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Public awareness of the degree to which human activity is stressing our biosphere is approaching the exponential phase of growth. Almost every day brings some jolting new example of the unyielding nature of the system that makes life possible, and with increasing bluntness we are forced to reexamine comfortable answers to questions long considered solved because our solutions have reappeared as new problems with completely unanticipated dimensions and persistence. Our technology has an excellent record of short-term gains, but our accounting system cannot deal with long-term costs. Land-based production efforts such as agriculture and intensive forestry are potentially vulnerable to our myopia in regard to this relationship. Many agricultural scientists have growing concern about our continuing capability to sustain soil productivity, and similar questions are being raised in relation to intensive forest management (Barber 1982). Furthermore, because forests cover such a large proportion of the land surface, it is only a matter of time before other ramifications of human activity, such as air pollution, significantly intersect and influence natural processes in forest ecosystems.

Symposia focused on forests and long-range air pollution have become at least annual events since 1975, and with each meeting we seem to be more convinced than ever that intersection has indeed already occurred. However, documentary evidence of adverse effects is, at this point, still not so overwhelming as to precipitate remedial action. The inertia of terrestrial systems and the unhurried subtle nature of forest growth have, thus far, not revealed undeniable symptoms of damage, so we continue to do nothing. Still, we have growing convictions that time-dependent consequences, whatever they are, will not be favorable or even neutral, and thus we are convinced that we should no longer persist in the notion that potential for damaging sustainability of forest ecosystem productivity does not exist. In this paper we will discuss possible interrelationships among air pollution, forest ecosystem productivity and forest management that we think have implications for forest management in northeastern North America. In the context of this discussion we emphasize acidic deposition resulting primarily from sulfur contamination of the atmosphere. However, as we all are well aware, air pollution is much more complicated than dissolving sulfur dioxide in water to form dilute sulfuric acid. Natural and anthropogenic additions to the atmosphere include many chemical elements and compounds, many of which have some potential for causing direct or indirect adverse influence on the forest ecosystem. Metal contaminants from fossil fuels released during combustion processes may be present in very small quantities, but they may accumulate in the soil system over long periods of time. We also need to remind ourselves that some contaminants may be viewed as beneficial. In many ecosystem nutrient budgets, precipitation nitrogen forms an important sustaining contribution to the total nutrient capital, and in some systems this may also be true for sulfur. Thus, there are many complex dimensions to the problem.

Many of the seemingly endless natural forests and grasslands that existed when Europeans first came to the North American continent have gradually been replaced by other vegetation systems. Some of these are similar to original communities while others are radical departures. In most cases the degree of departure from the original is closely associated with intensity of management. Experience with North American agriculture, which probably represents the most intensive form of large-scale land management, suggests that while increasing intensity of management usually means large increases in yield of the desired commodity, large energy costs for management are also incurred. Such costs arise from our attempts to compress the time scale required to attain naturally evolved equilibria of organic matter decomposition and nutrient transformation processes present in the forest or grassland community. There is also growing realization that these costs, expensive as they may be, cannot completely replace all natural phenomena ultimately involved in determining the productive levels of the original systems. As a result there is suspicion that productivities of many of our soils are, or soon may be, declining in spite of our best efforts to sustain them. Thus, as pressures to produce commodities increase, our capacity to supply these needed commodities may, in fact, be declining. While these trends are not as apparent in forestry as they are in agriculture, there is some evidence that changes in productive capacity can occur that have potential to reduce the growth of forest trees. In areas of the tropics including Borneo, the Far East and the Amazon Basin, growth decline in the second generation of plantations has been recorded (Mergen 1983), and similar situations have been documented in Australia (Farrell et al. 1981). Considering the advanced stages of mineral weathering in these tropical soils and the fact that most cases of second rotation decline involve exotic species, this phenomenon may not be surprising. For our temperate zone forests, including those of this region, there is a compelling body of evidence that nutrient removal from sites is greatly accelerated by intensive harvesting systems. In extreme cases rates of removal may be equal to that imposed by modern temperate zone agricultural systems such as corn (Boyle 1975).

For these reasons it is essential to consider first the effect that a given degree of forest management is imposing on a forest ecosystem so that potentially adverse effects of air pollution may be more clearly identified. Stone (1975) — speaking at the North American Forest Soils Conference at Laval University 10 years ago — described five categories of forest land use which impose different degrees of management intensity. These include remote wildlands such as occur in parts of Canada and Alaska which fall at or beyond the edge of the forest management spectrum. Protected wild forests are those set aside in parks, preserves and wilderness areas. It is probable that productivity in these two categories is being sustained by processes inherent in natural forest succession. Stone used the term "exploited forest" for those that are utilized by man with little or no investment of management effort except in extraction of wood or forage. Once extraction is accomplished, regeneration is left entirely to natural processes. Here changes in productive potential might occur as a result of the extraction process. These could be short term or long term in duration. In the regulated forest several silvicultural systems with a variety of objectives may be applied to assure regeneration control, species composition and stand density. Productivity is considered an inherent property of the site which can be degraded by unwise treatment or by fire.

The most extreme degree of management is found in the domesticated forest in which both genetic potential of the species chosen by the forester and the site potential itself are likely to be manipulated using large investments of physical inputs. In such cases, remarkable increases in yield have been achieved, but some authors consider that potential productivity of even these highly manipulated situations can be doubled by refinement of fertilizer prescriptions, control of competing vegetation, exploitation of nutrient, fertilizer and weed control interactions, and advanced tree breeding and tissue culture techniques (Farnum et al. 1983). Bengtson (1981) has urged foresters of the southeastern U.S. working with such systems to carefully consider needs for nutrient conservation in order to truly sustain long-term site productivity. The principles he articulates apply well to all intensive — domestic — forestry systems. Silviculture on this scale differs little from agriculture and horticulture, but, as Stone (1975) points out, the proportion of forest land in North America in this category is unlikely ever to be very large.

In all other management systems, if productive capacity is to be sustained, the forester must have a clear view of site-specific consequences of silvicultural practices and management objectives, particularly if management is based on economic and short-term yield-maximizing criteria rather than on ecological premises. Kimmins (1973a, 1973b, 1974) has underscored differences between the usual perception of sustained yield and the concept of what he calls the "ecological rotation", which is described as the period required for a given site managed with a given technology to return to the preharvesting condition. With our present deficiencies in ability to measure component processes of a forest ecosystem, it is probably impossible to determine exactly when preharvesting conditions have been or will be attained. In most cases, the time span for recovery is very likely to be greater than the number of years equal to the average age of the harvested stand. Time requirements for recovery are related to soil depth and to the nature of the bedrock, in addition to rates of atmospheric inputs of nutrients. Green and Grigal (1980) found nutrient accumulations in jack pine stands growing on deep soils to be greater than in stands on shallow soils. Granitic soils were observed to be low in Ca and Mg, and gabbro-derived soils were low in P. Stands on shallow soils had a greater proportion of total ecosystem nutrients in the vegetation than did stands on deeper soil. These authors concluded that removal of nutrients by timber harvesting may have more impact on nutrient status of stands growing on shallow soils than on those growing on deep soils. Weetman and Weber (1972) concluded that spruce stands growing on soils of marginal fertility may suffer from depletion of Ca, K and N when whole-tree logging is practised. These are precisely the kinds of situations which have been judged to be vulnerable to adverse effects of acid deposition resulting from air pollution (McFee 1980). When severe system disturbances, such as wildfire, whole-tree harvesting or site preparation via root raking or burning, remove vegetative cover and disturb or destroy the forest floor, such soils are exposed to the full impacts of acid precipitation and their vulnerability to change is increased.

In the last 20 years much progress has been made in developing a clearer quantitative understanding of how forest ecosystems function. Particular emphasis has been placed on determining nutrient budgets for these systems. With respect to sustained productivity, organic matter at or near the mineral soil surface is a sensitive indicator of ecosystem condition. This factor has long been recognized in a qualitative way by silviculturists, but the more recent work has made it possible to follow nutrient element dynamics much more precisely. In general, the picture that emerges is that productive capacity is an accretion process which, in a given climatic regime, is strongly correlated with the geologic nature of the substratum. Systems with soil parent materials well-endowed with inorganic nutrient elements will generally accumulate organic matter faster than those with parent materials poorer in nutrient elements. In either case the total nutrient capital in the ecosystem appears to continue to increase until a dynamic equilibrium is reached, at which time photosynthesis, respiration and all other metabolic processes of the ecosystem are more or less in equilibrium with other ecosystem processes. When this state is disturbed by harvesting, relationships among ecosystem components are changed and the process of reestablishing biotic regulation of movements of water and nutrients, nutrient storage, decomposition, mineralization and other pathways of energy and element movement and utilization begins anew.

Probably the most significant factor in the question of whether productive capacity of a particular site is being sustained or degraded is time. Productive capacity is a synonym for integration of all of the aforementioned interrelationships and equilibria. Not all of these are reached at the same time. Some require years and some require centuries, and with the present state of knowledge it is impossible to determine with any reasonable degree of precision when the preharvest state of balance has been reestablished. Instead, this decision is based on tree size or age, and, when some arbitrary state has been reached, the harvesting process is repeated. If this interval coincides with the time required for recovery of those equilibria that take longest to attain, then productivity is probably being sustained. But if, for example, a great deal of nutrient-bearing clay-size material is lost because of disturbances caused by harvest, and if the formation of clay takes centuries per gram, productivity cannot be sustained at the preharvest level unless the time between harvests is the appropriate number of centuries. Similarly, if the diversity of soil flora and fauna that are important in organic matter turnover is reduced by replacement of an equilibrium forest ecosystem with an exotic monoculture, the question of sustainability of productive capacity becomes even more complex and difficult to answer.

Neither is it sufficient to assume that if accurate accounts of the amounts of conventionally determined nutrient elements are made and if appropriate quantities of these elements are applied, that all will be well, no matter what harvesting interval is chosen. This Leibigian approach was not successful in agriculture, and it is less likely to apply to short-term silviculture, which is much more dependent on natural processes than is agriculture. If we accept the fact that, because of our ignorance of how productive capacity is maintained in forest ecosystems, and because of the pressures imposed by the current demands of society, it is likely that some forest harvesting as it is currently practised causes some reduction in theoretical site productivity, what then are the implications of acid deposition for forest management? As was stated in earlier discussion of this question (Voigt 1979), it is almost certain that sites on which short rotation harvesting is practised are more vulnerable to adverse consequences of acid deposition than are sites where ecological equilibrium is attained or where harvesting is done at intervals of 100 years or more. In most of the northeastern United States and Canada it seems unlikely that forest management will reach the stage that Stone (1975) labels domesticated forest, with attendant levels of management intensity. However, whole-tree harvesting with its impacts on ecosystem processes is a fact of life for forestry here, and other intensive management treatments are being developed and used.

The labels of exploited forests or regulated forests seem more likely to apply in the foreseeable future. Even, or perhaps especially, in such cases, considering the natural vulnerability of many of the soils in this region, the list of potential adverse effects on forest ecosystems is long; these have been addressed in other presentations in this symposium. The fact that we have known about acid deposition in degrees for nearly two decades in this region and have to this point been unable to ascribe direct growth effects to its influence suggests that, whatever the effects may be, they are more subtle than we suspected in the beginning. Nevertheless, the picture seems to be a little clearer now than in the past. We cannot ignore the studies of acidification of high-elevation Adirondack lakes which show a strong relationship between increased acidity and decreased fish population (Schofield 1976). These lakes do occur in a region of strongly podzolized soils, which might suggest that acid deposition at current rates of addition should have little effect. There are, however, other indications of change that could be related to increasing acidification. Decline in red spruce has been documented in Vermont (Siccama et al. 1982). Red spruce occurs at about 800 m in Vermont, and its distribution is believed to be related to the incidence of cloud moisture (Siccama 1974). Tomlinson et al. (1980) have shown that growing season cloud moisture has a pH between 3 and 3.5.

As more studies are made we shall be able to determine with increasing precision whether tree growth is adversely affected by acid deposition. Even if such direct correlations are not demonstrable in the near future, however, we shall still not be able to conclude that acid deposition and air pollution are harmless. It is entirely possible that a time frame similar to that described earlier for recovery of forest ecosystems may be required for detection of adverse influence of air pollution. If acid deposition increases leaching losses from living tree foliage, from forest floor material, from soil organic matter and from mineral soil, this complex process of increasing stress on the nutrient-supplying capability could be so slow that decades would be required to substantiate it. Similarly, if heavy metal contamination suppresses fungal metabolism so that organic matter decomposition rates are decreased and nutrient cycling slowed, the time required for detection could be even longer. A more serious consequence of protracted time spans for detection of potential adverse effects of air pollution deposition could be our inability to recover the original level of productivity once the effect of contaminants being deposited on the ecosystem is remedied. If certain key components of the ecosystem, such as fungal species, microfauna or macrofauna, have been eliminated or if their activities are altered so the original relationships among decomposing organisms no longer exist, then the whole pattern of organic matter decomposition could become more sluggish. This in turn could affect the well-being of primary producers, and eventually the forest could be quite different quantitatively and qualitatively.

In summary, there appear to be several forest management activities that have significance in considerations of effects of acid deposition in forest ecosystems.

Clear-cut harvesting of any kind removes the forest canopy, which is the first layer receiving deposition in the forest. If, in subsequent site preparation, understory canopy is removed and forest floor is disturbed or removed by burning or other treatment, the mineral soil will be exposed for some time to the full impacts of acid deposition. Whole-tree harvesting, whether merely concentrating slash in processing areas or removing all materials, leaves significantly less residue on the site to contribute to site resilience. In the western U.S., practices of piling, yarding and burning residues to facilitate planting and to reduce fire fuel loading are analogous to whole-tree harvesting in their impacts on site organic matter retention and recycling. We then have sites susceptible to impacts on soils, which have been discussed earlier. Obviously, the time of exposure of bare mineral soil to acid deposition is significant in this consideration.

Harvesting and postharvest treatments influence patterns of snow deposition, accumulation and melting. So, where acid accumulation in snowpacks is significant, there are potential interactions of harvesting and concentration of acid flush into soils or drainage systems (Overrein et al. 1980).

Species conversions from deciduous hardwoods to conifers have a variety of implications related to the chemistry of deposition materials reaching the forest floor and mineral soil. Because of conventional wisdom regarding species/soils compatibilities and because of economic pressures, it is most likely that such conversions will be prescribed for soils which are most sensitive to acid deposition. Conifers on such soils could increase site susceptibility to acid inputs and would almost certainly slow rates of forest floor decomposition and incorporation with mineral soil material.

If we procrastinate too long in applying what knowledge we have, we might find it necessary to use heroic levels of management intensity simply to get back to the level of forest productivity that once existed with no artificial energy inputs, and in some cases we may find even heroic measures too little too late. It will be a long time before such changes become visible even in the Northeast on a large scale, but when they do, recovery will cost much more than prevention will if we begin today.

Keen observation and broad experience can easily expand the list of combinations and permutations of silvicultural practices that can and may interact with the complex phenomenon of acid deposition. Generally, these involve acceleration of nutrient loss due to increased leaching and runoff and simplification of biological systems with concomitant reduction in buffering capacity. The challenge to each of us is to use our knowledge, wisdom and opportunities to influence and direct forest management policies and decisions in order to minimize actual as well as potentially harmful interactions. To paraphrase the words of Aldo Leopold, when we understand our lands and forests as communities to which we belong, we shall begin to use them with love and respect rather than simply regard them as commodities that we can use and exploit without wise and prudent stewardship.

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DISCUSSION

Question: Your conclusions suggest that we are being pushed into the traps of the industrial giants before we do anything about the problem. Comment?

Answer: I thought I made the case very strongly that we cannot, we simply cannot afford to wait for definitive proof before we do something about the situation. Who are the industrial giants? They are you and me as ratepayers of utilities, stockholders who demand profits from their investment. If you listen to experts like McFee and McClenahen, the information is pretty definitive that the probability of decline in forest productivity in relation to acid rain and its associated depositions is very, very high. We cannot afford the risk, that is my message. Aldo Leopold wrote something to the effect that one of the attributes of a good tinker is that he does not throw away any of the parts, and if we start throwing away some of the parts of our ecosystems, chances are we are going to lose some of the productivity.

Multiple Use Implications of Acid Rain and Forest Resources

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ABSTRACT

Ecological principles and research findings suggest ways in which acid deposition and other types of pollutants might influence amenity values of natural forest ecosystems. Illustrations of the responses of forest communities to high or intermediate pollution dosage show a general pattern of reduced species diversity and subsequent structural simplification. However, the stability of specific communities depends not only on pollutant dose, but on the nature of the ecosystem as well. Acid deposition and other pollutants may be slightly stimulatory or produce no perceptible effect where the dose is small or the ecosystem is complex and well-buffered (relatively resistant). Where the pollutant dose is large or the ecosystem is simpler or poorly buffered (low resistance), a significantly altered state may ultimately result. Measures of broader aspects of ecosystem functioning can give clues to eventual community changes, but may not reflect changes in special amenities such as the loss or reduction of rare species. It is proposed that the risk of altering natural terrestrial ecosystems through acid deposition or other pollutants, with attendant loss of amenities, will generally increase with the number of following conditions which obtain: (i) relict communities, major ecotones, or other community types growing near the limits of their natural range, (ii) communities containing a high proportion of specialists (usually late-successional), (iii) communities having potentially unstable mineral cycles (e.g., acid rain sensitive soils or those ecosystems that depend on rapid nutrient turnover to maintain productivity), (iv) communities subject to major additional disturbance by abiotic or biotic agents such as fire, harvesting, or insect and disease epidemics.

The topic of multiple use in forest resources is, of course, quite broad, including fiber production, wildlife, recreation of various sorts, grazing, and others. The basis for all of these potential uses lies in the nature of the forest ecosystem in regard to its structure, species composition, and functioning. This discussion will therefore focus on these kinds of responses of natural forest ecosystems associated with air pollution and acid deposition. Since the character of the community is an ultimate concern, emphasis will be on forest community dynamics. Theoretical considerations based on ecological principles and theory will be combined with pertinent research findings in an attempt to summarize what is known or predictable, and to point out important knowledge gaps.

Three hypothetical classes of pollutant dose relationship, proposed by Smith (1974), serve as a useful basis for discussion. His class I (low dose) situation occurs when the forest acts primarily as a pollutant sink and the ecosystem remains essentially unaltered or perhaps stimulated. An intermediate dose (class II) may create minor perturbations that may be detectable through subtle shifts in structure and composition, or in functional changes. Smith's class III relationship obtains when high pollutant dose directly induces tree mortality through severe physiological stress, leading to drastic alterations in community structure and succession.

Let us now consider the general nature of forest community response to pollution. Woodwell (1970) summarized this response from his own observations on oak-pine communities exposed to ionizing radiation, and the community changes reported for various other forest types subjected to strong local sources of air pollutants. The pattern of change begins with reduced species diversity, followed by successive removal of the vegetative strata from the tallest layer downward. This loss of standing crop is expected to ultimately result in loss of nutrient capital from the site.

Odum (1971), characterizing the response of complex natural ecosystems to pollution in terms of energy pathways, stated that "more energy is required for individual survival, diverting power that was formerly available for central organization and specialization. Such disturbed systems disintegrate with loss of specialists, and succession must start again with the generalized species".

This sequence of reduced diversity and structural simplification has been well- documented spatially in concentric vegetation zones outward from Woodwell's gamma radiation source, and along transects downwind from metal smelters. Vegetation in the vicinity of smelters in Canada's Sudbury region and elsewhere has been studied in particular detail (Gordon and Gorham 1963; Blauel and Hocking 1974; Wood and Nash 1976; Buchauer 1973; Jordan 1975). The assessment of community changes with distance from the Copperhill smelter near Sudbury by Freedman and Hutchinson (1980) illustrates the process for boreal forest exposed to a combination of SO_2, heavy metals, and acid mists. Beyond 22 km from the smelter, forests were dominated by conifers (*Picea glauca*, *Pinus strobus*, *P. resinosa*) and composition and structure were scarcely affected. Ground cover was continuous and contained species typical of the region. From 20 to 8 km from the smelter, forest cover remained continuous but less dense, and certain species were rare or absent from most sites (e.g., *Abies balsamea*, *Pinus strobus*). Likewise, the ground flora became depauperate, though mostly continuous. Between 3 and 8 km, only isolated forest stands occurred, these being restricted to sites protected from direct fumigation by smelter fumes. These isolated stands were dominated by species typical of earlier stages in the natural succession: *Populus tremuloides*, *P. grandidentata*, *Acer rubrum*, *Quercus rubra*, and *Betula papyrifera*. Ground cover was reduced to 7-20%, and grasses and other "weed" species dominated. Sites closer than 3 km were either bare or, in less-exposed situations, supported grasses and a few herbs and scattered low-growing woody plants. Nutrients and, in fact, soil itself had been lost from many areas near the smelter due to removal of vegetation, creating sites where only the long process of primary succession can take place following reduction of pollutant emissions.

Can air pollutants and/or acid deposition at moderate or low dosages induce similar changes, and are such effects likely to follow the classic pattern hypothesized by Woodwell (1970) and illustrated by the preceding studies? Are certain forest ecosystems less stable than others, and hence more susceptible to acid rain and other moderate pollutant dosages? What changes are most likely to occur under such dosages? These issues will now be considered.

One approach to assessing forest community changes due to moderate air pollution stress is the use of simulation models. Models allow long-term results of pollutant stress to be predicted, and they facilitate understanding of the processes involved (Kickert and Miller 1979; Shugart et al. 1980). Two recent modeling efforts illustrate this approach. In the western U.S., the influence of SO_2 on mixed conifer forest growth and succession was investigated using a simulation model (SILVA) that included effects of fire, moisture stress, seed production, and episodic or chronic pollution dosage (Kercher et al. 1980; Kercher and Axelrod 1982). A similar model was used to examine SO_2 effects on a mixed deciduous forest in eastern U.S. (West et al. 1980). In each case, differential growth stresses were applied to individual species based on their known sensitivity to SO_2. The models revealed long-term changes in composition of tree species to be expected under given conditions of environment and pollutant stress. A similar approach, using or adapting existing models such as these, could be used to estimate long-term consequences of acid deposition, the detection of which may be extremely difficult or impractical by direct observation. However, such models may not provide the necessary detail on attributes relating to certain values; the fate of shrubs or herbaceous species which may contribute greatly to the aesthetics or wildlife habitat of a particular forest landscape remains unresolved unless these components are specifically included in the model.

Case studies provide direct evidence of pollutant effects on forest ecosystems, and they can collectively indicate a range of expected responses for different environments and types of vegetation. Unfortunately, only a few community- or ecosystem-level studies have been conducted under conditions analogous to Smith's (1974) low or intermediate pollutant dose; none have been done specific to acid deposition. Such dosages of oxidant and/or SO_2 have been implicated in the decline of white pine and reduced productivity of meadow communities in Virginia (Duchelle et al. 1980; Skelly et al. 1979), decreasing species richness and retrogression in California drought-deciduous shrublands (Westman 1979), a general decrease in diversity and marked shifts in understory community composition in a Canadian boreal forest (Scale 1980), and reduced species diversity and richness in a Pennsylvania mixed deciduous forest (Rosenberg et al. 1979).

In the northern Rocky Mountains, Harward and Treshow (1975) and Treshow and Stewart (1973) conducted field and laboratory ozone fumigations of aspen community vegetation. They concluded from sensitivities of certain species that significant species shifts in the understory community would occur with ozone levels only slightly above ambient for the region.

An excellent example of a temperate forest community growing in a relatively stable, unchallenging environment is the mixed mesophytic forest type in the east-central U.S. These forests occupy coves and protected sites where temperature and moisture stress are moderate and soils are well-drained and rich in nutrients. The mesic environment is conducive to the development of a highly diverse, structurally complex community (Braun 1950). This habitat supports a high proportion of specialists (K-selected strategists), many of which have relatively narrow ecologic amplitudes. These communities offer a unique opportunity for examining both ecosystem and individual species responses to introduced environmental stress such as air pollution.

Studies of this type were conducted in mixed mesophytic forests of the Ohio River Valley in southeastern Ohio, U.S.A., along a gradient of industrial air pollution (McClenahen 1978, 1980). The gradient of pollutants, which included sulfur oxides, chlorides, and fluorides, was considered to lie within Smith's (1974) intermediate-to-low dose range. These mature communities contained at least 19 tree species in the forest canopy, and as many as 50 species in the herb layer; a total of 124 species of higher plants were encountered on sample plots within the seven stands investigated.

Shannon diversity was found to be generally reduced in stands receiving highest pollutant exposures (Fig. 1); however, this was primarily due to concentration of dominance (lower evenness) rather than reduced richness. Evidence of structural simplification was found only in the canopy layer, where density was strongly and negatively correlated with increasing pollutant exposure (Table 1). Within the overstory, *Acer saccharum* Marsh. and *Fraxinus americana* L. density seemed most adversely affected by pollutant exposure, but *Aesculus octandra* Marsh. apparently tolerated the pollutant regime. Other strata were either scarcely affected or total abundance increased.

The maintenance of understory structure appeared to be largely due to shifts toward dominance of a few species which were apparently tolerant of the pollutant dosage. In particular, *Lindera benzoin* (L.) Blume, *Staphylea trifolia* L., and *Hydrangea arborescens* L. became much more abundant in the shrub layer of higher-exposure communities, whereas the typical dominant, *Asimina triloba* (L.) Dunal, decreased. In the herb layer, *Impatiens* spp. (*I. capensis* Meerb. and *I. pallida* Nutt.) and possibly *Phlox divaricata* L. responded positively to increasing pollutant exposure. Several herb species showed notable declines in abundance: *Pilea pumila* (L.) Gray, *Arisaema strorubens* (Ait.) Blume, *Hydrophyllum appendiculatum* Michx. (Table 1).

Competition with increased numbers of understory shrubs and herbs in the high-exposure stands may be partly responsible for observed decreases in woody reproduction. Correlation analysis indicated that abundance of understory *Acer saccharum* Marsh., *Fraxinus americana* L., and *Ulmus rubra* Muhl. generally decreased in the shrub and herb layers with increasing pollutant exposure (Table 1). This reduced reproductivity may contribute to ecosystem instability (Smith 1980).

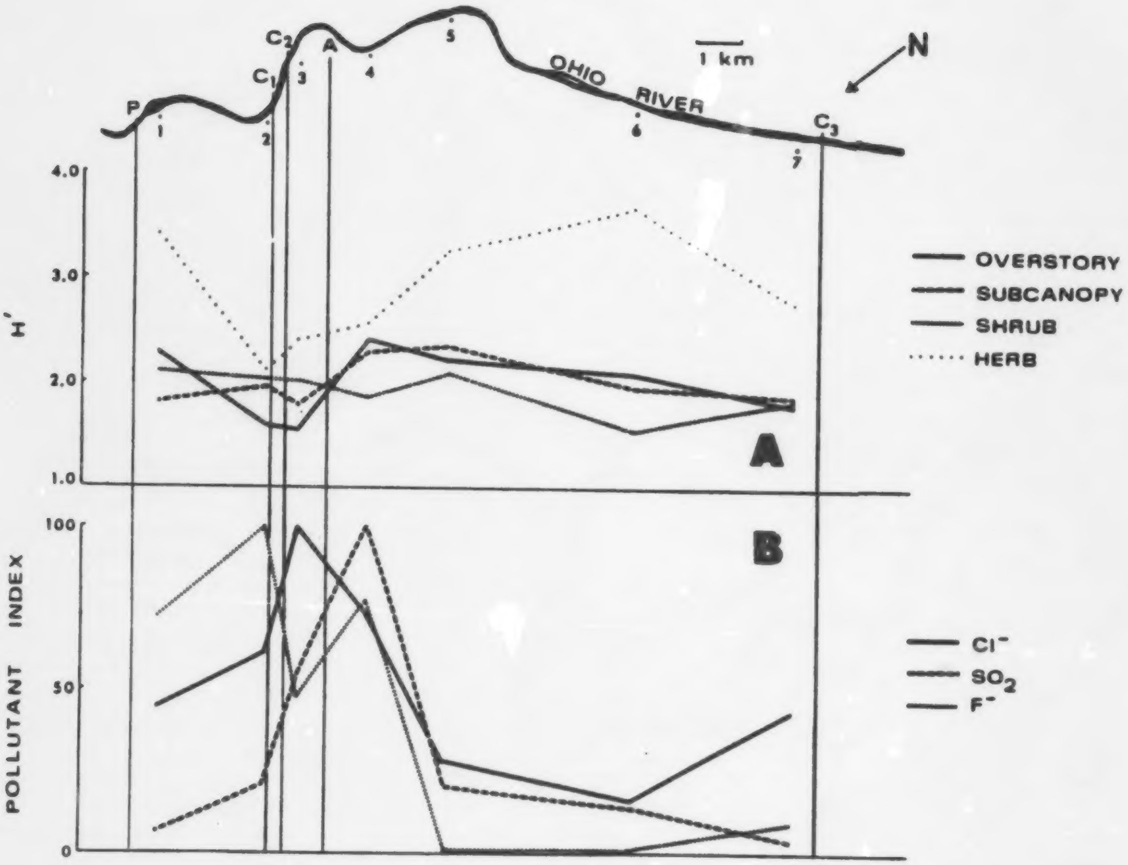

Figure 1. Gradients of (A) Shannon diversity index (H') for various forest strata and (B) relative air pollutant indexes for chlorides (Cl^-), sulfur dioxide (SO_2), and fluorides (F^-) measured in seven stands in the Ohio River Valley. Numbered stand locations and major industrial air pollutant sources are shown at the top of the figure. Pollutant sources are identified as P (coal-burning power plant complex), C_1, C_2, and C_3 (chemical plants) and A (aluminum reduction plant). The river flow is southerly (from McClenahen 1978).

Table 1. Correlation of abundance (woody plants) or percent cover (herbs) of major species with index of relative exposure to air pollutants in the Ohio River Valley[1]

Species	Vegetative layer			
	overstory	subcanopy	shrub	herb
		-r-		
Acer saccharum Marsh.	-0.96*	-0.72*	-0.86*	-0.75*
Aesculus octandra Marsh.	0.22	-0.38	0.03	--
Fraxinus americana L.	-0.31	-0.20	-0.14	-0.27
Ulmus rubra Muhl.	0.39	0.53	-0.60	-0.11
Asimina triloba (L.) Dunal	--	0.22	-0.62	0.12
Lindera benzoin (L.) Blume	--	0.85*	0.86*	0.16
Staphylea trifolia L.	--	--	0.67*	0.40
Impatiens spp.	--	--	--	0.68*
Pilea pumila (L.) Gray	--	--	--	-0.76*
Arisaema atrorubens (Ait.) Blume	--	--	--	-0.50
Hydrophyllum appendiculatum Michx.	--	--	--	-0.69*
Total woody stems	-0.75*	0.70*	0.38	-0.65
Total % herb cover	--	--	--	0.53

[1] For explanation of air pollutant exposure index, see McClenahen 1978.

* Significant at P=0.05.

There is evidence that community composition has also shifted in relation to the pollutant gradient (Fig. 2). Similarity of stands in terms of species present on quadrats was compared by coefficient of community (Pielou 1975) against the species complement of the least-exposed community. More detailed analysis by strata indicated that the shrub and herb layers differed most in composition along the gradient. There were 20 and 22 herbaceous species exclusive to quadrats in the low-exposure (three stands) and high-exposure (four stands) areas, respectively. Of the woody species, six and three were respectively exclusive.

The apparent sensitivity of understory vegetation to pollutant gradients suggests lower strata especially should be examined for early, subtle signs of pollutant-induced changes in future studies (Rosenberg et al. 1979; McClenahen 1978).

Mineral cycling also appears to have been altered along the pollutant gradient (McClenahen 1980). In particular, comparative rate increases in both input and throughfall of SO_4^{2-}, NO_3^-, Ca^{2+}, Cl^-, and F^- were found in the region of high exposure. These pollutant-associated rate changes in element cycling can be viewed as a functional destabilization (Jordan et la. 1972; Webster et al. 1975). There is a concern that functional instabilities may translate into significant community changes following complete harvesting, fire, or other drastic disturbance. However, cause and effect links with community stability have not been established. This is an important knowledge gap in connection with the acid deposition phenomenon, because functional destabilization is frequently implied or suggested as a mechanism for creating community instability as well.

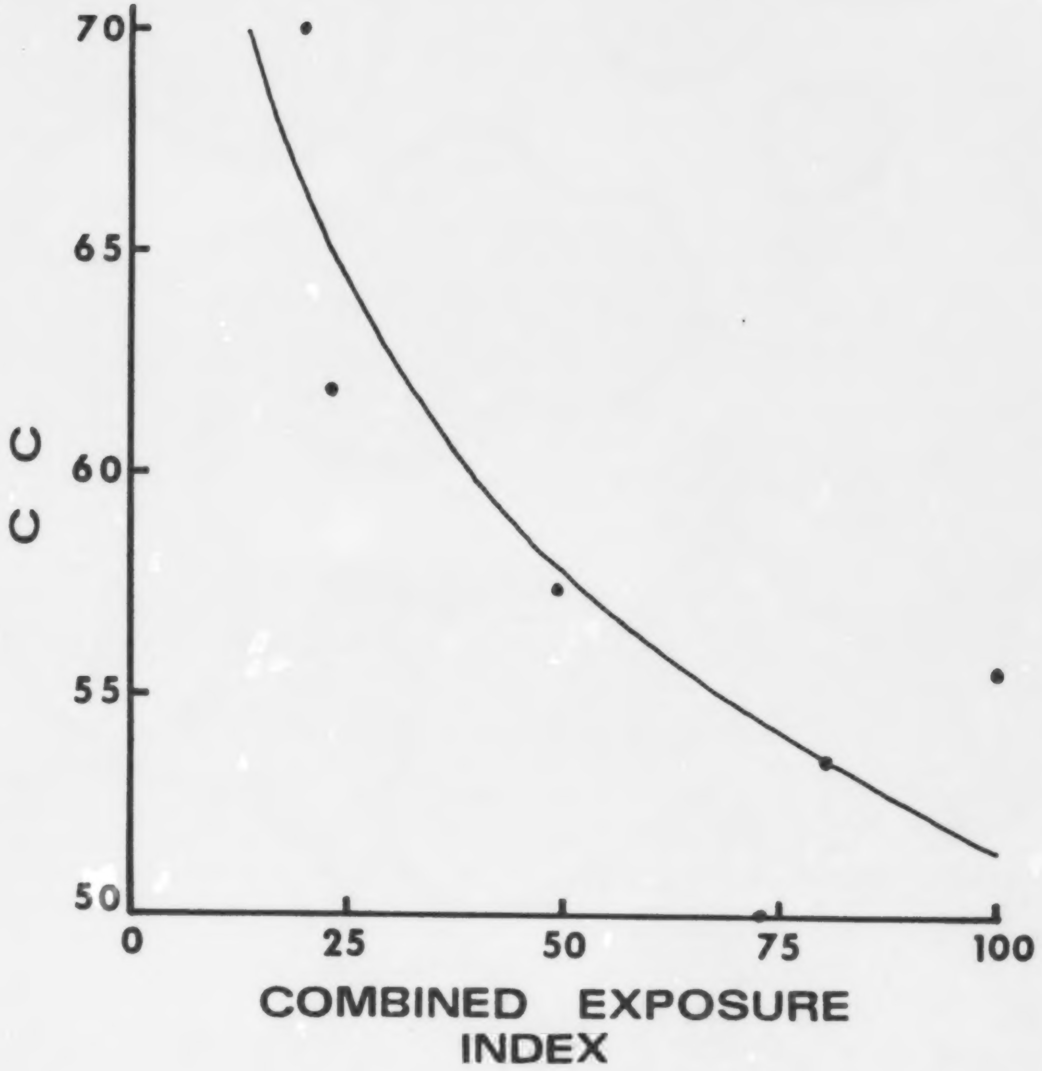

Figure 2. Relationship of coefficient of community (CC) and combined air pollutant exposure index. CC is an index of similarity in species composition between two communities, i.e., higher values of CC indicate greater similarity. Equation for the curve is CC = 93.48 - 21.03 $\log_{10}$ (combined air pollutant index); r = -0.88 (from McClenahen 1978).

The studies just discussed seem to indicate that moderate pollutant stress can influence forest community dynamics. Studies in Ohio River Valley mixed mesophytic communities suggest that increasing dominance of pollutant-tolerant species can act as a buffer against structural degradation. It is hypothesized that the apparent buffering capacity of these communities arises from the inherently low environmental stress associated with mesic sites which, in turn, mediates high species richness. Although greater richness increases the probability of types that can be selected for pollutant stress tolerance, a favorable (e.g., mesic) environment is probably the basis for this buffering capacity. Along with reduced diversity in the lower strata due to pollutant exposure, shifts in species composition were greatest in these strata as well. Thus, changes in understory competitive relationships mediated by pollutant stress seem to have resulted in species replacement rather than further structural degradation. Similar increases in understory flora were observed at a point along a pollutant gradient where canopy tree density initially declined (Scale 1980), and in wind-regenerated balsam fir forests in New England (Sprugel and Bormann 1981). In the latter case, overstory degeneration brings with it increased community net productivity due to rapid understory growth. This high productivity and apparent luxury consumption of nutrients by the understory help conserve minerals that might otherwise be lost, thus imparting resilience to the ecosystem.

A similar process of nutrient conservation can be hypothesized for pollutant-disturbed forests of the Ohio River Valley and elsewhere. The extent to which such communities under a given pollutant stress are able to buffer against degradation may relate to the interrelationship of environment and community. Mesic sites generally support the most complex, species-rich communities and may therefore have the greatest capacity for buffering against structural change (resistance). Forest ecosystems occupying sites which are wetter, drier, nutrient-limiting, or otherwise more environmentally stressful generally are also less complex and may therefore be less tolerant of pollutant stress. There is evidence of differential tolerance associated with site/community relationships near the smelter complex at Sudbury (Freedman and Hutchinson 1980). However, survival of isolated forest communities in the high-impact zone has been ascribed in part to lower exposure on these more sheltered sites.

In the final analysis, it seems advisable to assess the sensitivity of ecosystems to acid deposition or gaseous air pollutants using a much broader basis than substrate characteristics alone. An ecological approach has been proposed (Cowell et al. 1981), and the incorporation of forest community type in acid deposition sensitivity ratings has been attempted in Canada (Robitaille 1980).

Present knowledge of ecosystem effects of pollutant stress and use of ecological concepts can provide a rational basis for developing criteria. It is proposed that natural forest ecosystem sensitivity to alteration by acid deposition or other pollutants will likely increase with the number of following attributes which obtain: (i) relict communities, major ecotones, or other community types growing near the limits of their natural range, (ii) communities containing a high proportion of specialists (usually late-successional), (iii) ecosystems having potentially unstable mineral cycles, such as those with acid rain sensitive soils (Cowell et al. 1981) or relatively rapid nutrient turnover rates, (iv) communities subject to major additional perturbation by abiotic or biotic agents such as fire, harvesting, or insect and disease attack.

How might the diverse uses of forests be influenced by pollutant-mediated community changes? First, many of the community types judged to be sensitive by the above criteria possess the most interesting and aesthetically pleasing vegetation. Certain of these communities are considered unique or rare and are specifically preserved or protected. The loss or decline of a specially valued component can have significant aesthetic impact, even though the effect on the ecosystem may be unimportant.

Second, some components of an ecosystem may resist perturbation at the expense of other components. Such may be the case in the mixed mesophytic forest described earlier. The apparent capacity to resist structural degradation stemmed from concentration of dominance among pollutant-tolerant types and partly by species replacement, thus reducing both total richness and the abundance of certain species. The utility value of the altered community may have declined with the decrease of *Acer saccharum* and *Fraxinus americana* while certain wildlife values may have benefited through increased understory density. It is therefore important to remember that pollutant-induced, moderate alteration of forest ecosystems will likely have both positive and negative aspects from a multiple-use perspective.

Within regions having actual or potentially elevated levels of ambient air pollutants and/or acid deposition, research should be especially directed toward forest ecosystems deemed most sensitive and of greatest economic or aesthetic value. Correct identification of sensitive ecosystems requires a more comprehensive assessment approach, one that utilizes both environmental (site) and community data. The complexity of these ecosystems and the suspected subtle, long-term nature of potential pollutant effects demand a truly integrated research approach combining field and laboratory studies and simulation modeling.

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DISCUSSION

Question: I presume from your talk that you would consider a sugar maple stand that had all the non-maple species removed as being more sensitive to air pollutant stress. Comment please?

Answer: I was using that example to demonstrate some general responses. I did not presume to rate or set up a specific rating system. There is quite a mixture of pollutants in that particular situation, chlorides, fluorides, sulfur oxides, ozone all high at some point along the gradient. In that particular situation the response was so dramatic that I think a pure sugar maple stand there would have been completely changed, very quickly.

TECHNICAL SESSION IX
CLOSING ADDRESS

Closing Remarks

F.L.C. Reed, Assistant Deputy Minister
Canadian Forestry Service
Ottawa

First, I should like to convey my thanks and congratulations to Dr Gilbert Paillé, Director of the Laurentian Forest Research Centre, and to each member of his Conference Steering Committee. In the last few days these people have earned our respect, admiration and our profound appreciation for having organized an extraordinary Conference in terms of content, style and organization. Good humour and sustained interest have been evident in this room right up to the last afternoon. I think it would be perfectly in order right now to give these people a big round of applause. I extend my personal thanks also to the co-sponsors and collaborators. Especially valuable was their support and their wise judgement when the program was designed, when the speakers were chosen, and when every detail of the program was determined.

I am also delighted to see the private sector here in such numbers. This is something new in Canada, where the private sector is taking a very keen interest in a subject which at times seems esoteric. Nevertheless, they persevered and I am grateful to them for having stayed to learn with us. Nor can we forget 235 delegates from eight countries; all from diverse and related fields, and they have felt at home in Québec. I want to thank the people of Québec who put this on. I have never come to a conference in Québec that I did not enjoy immensely. You must all come back next year to the big Joint Conference of the Society of American Foresters and the Canadian Institute of Forestry.

With regard to the subject matter of the Conference, I sense that you have made impressive gains in knowledge since 1975. Ignorance is being conquered and you have made a great leap forward. But you still have no consensus yet on the magnitude of the threat from acid rain on the forests of North America; certainly not in Canada. However, there is a consensus, namely in the measurement of the reduction of growth and yield arising from neglecting forest renewal, from not replanting after harvesting, and from the losses caused by insects, diseases and fire.

Decisions on forest renewal are easy, by comparison. We do not have a choice; we have to move ahead very quickly. The undivided attention is required of the land manager, the senior officials like myself, and of the elected representatives from the states, provinces, Parliament or Congress. There is no other choice but to manage the land. So while the scientific community is working feverishly on acid rain research, I shall be planting and tending trees and fighting fires and insects, waiting for you to catch up. Personally, I wish you well. You have my confidence and encouragement. I should like to see the resources of scientists here doubled. Maybe we shall live that long to see it.

In closing, may I underline my feelings on the whole subject of forestry and forest science with a few words of poetry which some of you may have heard me quote before? They are from Robert Frost, who wrote a beautiful little poem called "Stopping by Woods on a Snowy Evening" He said:

> "The woods are lovely, dark and deep, but you have promises to keep, and miles to go before you sleep".

Miles to go before you sleep!

Thank you very much, Mr. Chairman.

TECHNICAL SESSION X
INTRODUCTION TO FIELD TOUR OF CATCHMENT BASINS

The United States Experience in Using Experimental Watersheds in Acid Rain Research

Robert S. Pierce
Northeastern Forest Experiment Station
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Scattered throughout the United States are about 100 experimental watersheds that have been established and are being operated by a variety of federal and state agencies, educational institutions, private industries, and foundations. These watersheds have long been studied to determine their hydrologic characteristics as influenced by natural and human-induced changes. Information from such research is used to guide land-management practices. Because the acid rain phenomenon is a fairly recent concern, it is doubtful that a large number of experimental watersheds are being used to study acid rain; certainly, few are devoted exclusively to acid rain research. This conference focuses on the possible impacts of acid rain on forests, so my comments deal with forested experimental watersheds. And because most of these watersheds in the United States are operated by the USDA Forest Service, I shall describe the acid rain research programs under way on them.

The Forest Service currently operates six experimental forests (that include clusters of experimental watersheds) where research on atmospheric deposition is being conducted. Forest Service scientists also participate in the National Atmospheric Deposition Program at these experimental forests and at five other sites.

Traditionally, experimental watersheds established by the Forest Service are used for determining water budgets, erosion, production of stream sediment, and forest growth resulting from some form of land manipulation. Because they can never be replicated exactly in time or space, the research design on these experimental watersheds requires unusual statistical approaches to interpret study results. Commonly, watershed parameters such as precipitation and streamflow are continuously measured simultaneously (calibrated) on at least two nearby watersheds for 5 to 10 years. Then one watershed is treated and the changes, if any, are compared with those on the untreated watershed.

In the last 20 years, forest watershed research has expanded beyond comparing simple water quantity budgets to using small experimental watersheds to evaluate complex biogeochemical processes. The same paired watershed approach is used with several years of pretreatment data gathered, but the magnitude of the data taken is enlarged enormously. Researchers in an array of disciplines, e.g., soils, meteorology, aquatic biology, chemistry, forest ecology, and animal behavior, are sought and encouraged to concentrate their research efforts on such watersheds.

An arrangement that has proven valuable is for a federal agency such as the Forest Service, which has management responsibilities for large blocks of land (in this case, suitable forested watersheds), to join forces with universities with faculty members with varied backgrounds, graduate students, and their own sources of funding. A case in point is the Hubbard Brook Experimental Forest near West Thornton, New Hampshire, where Forest Service scientists have worked in cooperation with researchers from Yale and Cornell Universities, Dartmouth College, New York Botanical Garden, and many other educational institutions and agencies for more than 20 years. The Forest Service provides the continuity of land ownership, management, responsibility for coordination, and research in specialized fields, while the cooperating institutions and agencies provide augmentation in many other disciplines, short-term studies, and new ideas generated by graduate students. At Hubbard Brook, a series of nine experimental watersheds ranging from 12 to 76 hectares have been operating from 14 to 27 years. An enormous body of information has been collected on almost every aspect of these watersheds, including biogeochemical data on soils, vegetation, climate, streams, and animals. The sharing of information among active researchers at Hubbard Brook has resulted in the emergence of a comprehensive understanding of the flux of energy, water, and nutrients in northern hardwood forest ecosystems.

What has all of this to do with acid rain and experimental watersheds? The longest continuous record of precipitation chemistry in North America (20 years) has been acquired at Hubbard Brook. The recording of these data did not begin as part of research concerning acid rain, but was an essential component of the biogeochemistry data base of the northern hardwood forest ecosystem (acid rain was an unfamiliar term in the United States 20 years ago). Yet this record has become one of the most valuable pieces of available information pertinent to long-term trends of atmospheric deposition.

In time, other parameters that are being monitored in the watersheds, such as soil nutrient levels, tree growth, diversity and distribution, and stream water chemistry and biology will provide necessary benchmarks for future comparisons of potential impacts of acid rain on forest ecosystems. Some watersheds are being examined to determine if the combined effects of tree removal, as practised in whole-tree harvesting, and acid rain may exacerbate the potential influences of atmospheric deposition on forests.

At most of these experimental watersheds, intensive studies of processes (e.g., soil water/nutrient movement) are being investigated on small plots where conditions can be controlled. Once the basic processes of the flux of water, nutrients, and energy for such plots are better understood, simulated acid rain experiments can be imposed on the plots to observe possible changes. Adjacent watersheds with physical features (e.g., soil, vegetation, climate) similar to the plots can be used for comparison and confirmation. Experimental watersheds can be important in acquiring necessary information about forest ecosystems beginning with (1) a hypothesis; (2) testing this in highly controlled laboratory situations; (3) further testing in the field on small plots; (4) expanding the scope to uniform treatment of an entire watershed; and (5) observing natural untreated or treated systems to compare information in steps 2-4.

The apparent decline of forest growth in Europe, the northeastern United States, and eastern Canada has been noted by changes in tree-crown health and tree-ring width. If atmospheric deposition proves harmful to forest growth, it is likely that it also will have detrimental effects on other forest environmental characteristics such as soil, fauna, vegetative ground cover, and streams. Detection of possible effects of atmospheric deposition on these features singly may be extremely difficult. However, the combined effects (e.g., soil and vegetation) may cause pronounced changes in the environment as seen perhaps in parameters of stream water. Small experimental watersheds offer a way to evaluate the amalgamated effects of many environmental impacts on forests.

We are continually putting out brush fires! A few years ago forest managers and the public were embroiled in the emotional clearcutting issue. Last year, the gypsy moth was a serious economic problem. Today, acid rain is THE hot political target. Tomorrow it may be hazardous waste disposal or water shortages or some other pressing social concern involving forest lands. One approach to solving these extremely difficult environmental problems is to gain an understanding of the nature, extent, and interrelationships of the major processes involved in natural systems. For forest ecosystems, small experimental watersheds can offer unique opportunities to examine these processes in detail within their boundaries, and then compare the results with those on other pieces of landscapes with somewhat similar attributes. Also, long-term records of soil, water, vegetation, and climate in experimental watersheds provide the priceless historical documentation that is necessary for detecting changes in present-day environments.

Field Tour and Catchment Basin Approach: Canadian Experience

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Canadian Forestry Service
Ottawa

The purpose of these few remarks is to explain why we are using the catchment basin approach in the Canadian Forestry Service (CFS) Long-Range Transportation of Air Pollutants (LRTAP) Program. Such an approach is costly, so why are we using it? What can it tell us, and where does it have to be supplemented by other types of studies?

As a prelude, I might say that CFS studies with air pollution go back a long way — to the situation in Trail, B.C., in the 1930s, to Sudbury, Ontario, in the 1950s, and more recently to numerous other strong point-source situations where high ambient concentrations of sulphur dioxide brought about dramatic effects on forest growth.

In such heavily polluted localities research studies are able to identify a number of features characterizing stressed vegetation and soils. Tissues can show chlorosis and necrosis, and sulphur contents can be elevated. Growth rates can be depressed, and it is possible to rank different species in susceptibility. Perhaps most important, with the help of fumigation chambers, threshold ambient concentrations of pollutants can be specified as guides to regulatory standards and abatement targets. In some cases, the sulphur and heavy metal contents of soils are dramatically increased.

When, in the 1970s, the CFS and others began to design studies suitable for the investigation of acid rain and LRTAP, the limited available experience suggested the phenomenon and its manifestations might be rather different. Conventionally viewed phytotoxic concentrations of pollutants would be absent, elevated sulphur contents of tissues might be difficult to discern, visual symptoms were unknown, but some longer-term growth effects were thought likely, through basic growth processes being impaired.

In contrast to this somewhat enigmatic and elusive situation, that for soil seemed clearer. Additions of acid sulphate might have little effect in the short term, but sooner or later unwelcome changes could occur through accumulation. Soil acidity could be increased, potentially toxic elements mobilized and the normal leaching of plant nutrients accelerated. Desirable micro-organisms could be weakened. Overall, site fertility could be irreversibly lowered. What was completely unknown was the nature and rate of such soil degradation processes on different soils under different pollutant loadings.

To come to grips with this problem, the available experimental approaches had both strengths and weaknesses. The often successful approach of comparing a treated or affected field site with a control was excluded because of the necessary distance involved and the necessary latitudinal orientation of treatment and control sites. The comparison could be invalidated by parallel differences in climate, vegetation, soils and surficial deposits that had nothing to do with pollution.

The use of simulated acid rain of different strengths with both plants and soils under carefully controlled greenhouse conditions had greater potential for accelerating a long-term process. With plants the more immediate seasonal effects might be revealed and with soils possible longer-term changes.

For soils the approach follows the familiar lysimetric approach, the limitations of which are fairly well known. Perhaps the most serious of these is extrapolation of results obtained from a reconstructed monolith to the field. Both have the limitation of not providing field sites the properties of which can be characterized and used as a datum against which future pollution effects can be measured.

It is perhaps not surprising, therefore, that the catchment basin approach as used so successfully by hydrologists should have particular appeal. A few well-chosen and representative catchment basins straddling the acid-rain impact zone of eastern Canada could serve to focus the efforts of meteorologists, forest scientists, hydrologists, fish biologists and wildlife specialists who often have need of similar background information or could expedite their progress by pooling data.

Moreover, the basins could serve as reference points and, if maintained over a reasonable run of years, could do much to indicate long-term trends, as well as shorter-term cyclical changes and the periodicity and amplitude of unusual years. Perhaps, equally important for a stress of unknown dimensions, catchments permit what has been called the biogeochemical approach, where the inputs and outputs of pollutants can be studied in relation to other cycling budgets and to a variety of more specialized processes and transfers of materials.

For the forestry sector, it is possible to take very precise pollution input data provided by the meteorologist, to measure entrapment, interception, and stemflow by the forest canopy and the effects of these processes upon tree tissues. Similar absorption and release exchange processes can be measured in the litter and soil horizons and drainage waters analyzed for loss of materials from the system. At this point the interests of the hydrologist and fish biologist commence.

In the least complex elaboration, therefore, an input-output model for water quantity, nutrient budget and sulphate fate can be developed for each catchment. And it is claimed by some that this can be further elaborated to include the response of tree growth and the effects of pollutants.

Whether this is, in practice, attainable within a reasonable time frame is debatable, but the fact remains that a catchment with its biogeochemical approach does provide essential information about a unit of natural landscape. This includes the important aspect of retention or transmission of sulphate, likewise for nitrate, and likewise for heavy metals. In addition, the catchment is able to provide a range of plant and soil materials for process studies about which much else is known. Successive studies in different disciplines can capitalize on the accumulated wealth of past studies.

Where a catchment has limitations, however, is in uncertainty associated with its representativeness, in the stability of the observed "equilibrium" between the forest cover and the soil, and in a catchment's inability to incorporate different degrees of pollution stress or to include unstressed controls. The biogeochemical approach by itself seldom tells us how quickly a system is degrading or by how much a stress must be decreased to reduce change to an acceptable rate.

Some of these limitations can be reduced, others cannot. For example, by a very careful analysis DOE scientists have selected three main forested catchments in sensitive areas that cover a range of deposition levels going from medium/low, through medium/high to medium. All soils are podzols or brunisolic with climatic characteristics broadly similar except for the maritime influence in the Kejimkujik basin. The vegetation ranges from maple-birch, through spruce-fir boreal to mixedwood. The three basins are supplemented by satellite sites in Manitoba and Newfoundland where less comprehensive studies are in progress.

Taken collectively, as an entire suite, these sites can suggest the influence of pollution on vegetation and soil properties, not obtainable from a single catchment. Such properties would include elevation of foliar sulphur contents, soil-sulphur make-up, fulvic/humic acid balance of soil organic matter, exchangeable base status and heavy metal content. Such an approach does mean, however, that methodologies should be comparable and comparisons among catchments made.

Shortly you will be seeing the research installations set up in one of our three catchment basins. This is a medium to heavily impacted part of the typical eastern Canadian spruce-fir boreal forest. There, first-hand, you will learn of the studies in progress. It should not be forgotten, however, that elsewhere in the field and in the laboratory and growth chamber there are process studies that supplement the framework biogeochemical studies. Some of these are described in papers and posters presented at this Conference. They include studies in soil-nitrogen transformations, the testing of seedling development, pollen viability and mycorrhizal development to simulated acid rain of different strengths, the development of tree sensitivity criteria, and the distribution and interaction of heavy metals with soils and plants. All are contributing to an early elucidation of the dose/response relationship which has to underpin the specification of ceiling pollutant levels.

Lake Laflamme Catchment Basin: Excursion Guide

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REGIONAL PERSPECTIVE

The Lake Laflamme catchment is situated 80 km north of Québec City on the site of the Montmorency Experimental Forest, Laval University. The 825 m rise between these two points causes an environmental gradient strong enough to delimit several vegetation zones (Fig. 1).

Vegetation

Sugar maple-basswood zone*

Altitude: below 100 m. Soil type: sombric brunisol. Climax association: sugar maple with basswood, white ash, ironwood, northern red oak and white elm. Associated shrubs: *Dirca palustris, Sambucus pubens, Corylus cornuta, Cornus alternifolia, Lonicera canadensis*. Associated herbs: *Asarum canadense, Caulophyllum thalictroides, Adiatum pedatum, Aralia racemosa, Dicentra cucullaria, D. canadensis, Claytonia caroliana, Smilacina racemosa, Trillium erectum, Hydrophyllum virginianum, Erythronium americanum, Polygonatum pubescens*. Particularities: once covered with deciduous forest; is largely cleared and cultivated; is second growth forest; mosses almost absent.

Sugar maple-yellow birch zone

Altitude: 100 to 300 m. Soil type dystric brunisol Climax association: a deciduous forest dominated by sugar maple, yellow birch, beech, with some red spruce and hemlock. Associated shrubs: *Sambucus pubens, Cornus alternifolia, Lonicera canadensis, Viburnum alnifolium, Acer spicatum* and *Taxus canadensis*. Associated herbs: geophytes common to all maple forests. Particularities: appearance of acidophilous herbs such as *Dryopteris spinulosa, Oxalis montana, Lycopodium lucidulum, Clintonia borealis*, and *Maianthemum canadense*. Mosses include *Dicranum* spp., *Mnium* spp.

Balsam fir-yellow birch zone

Altitude: 300 to 600 m. Soil type: minimal podzol. Climax association: a mixed forest of balsam fir, yellow birch with red spruce, white spruce and white birch. Associated shrubs: abundant *Acer spicatum* with *Viburnum alnifolium, Corylus cornuta, Taxus canadensis, Sambucus pubens, Sorbus decora*. Associated herbs: acidophilous species. Particularities: important source of sawlogs and pulpwood. Mosses not plentiful.

Balsam fir-white birch zone

Altitude: 600 to 900 m. Soil type: ferro-humic podzol. Climax vegetation: a balsam fir-white birch-*Dryopteris spinulosa* forest with white spruce and mountain ash. Associated shrubs: the common shrubs are *Acer spicatum, Lonicera canadensis, Viburnum edule, Sambucus pubens*.

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* The vegetation zone descriptions taken in part from the Fourth North American Forest Soils Conference. A visit to Montmorency Forest. Laval University, Québec, 37 p.

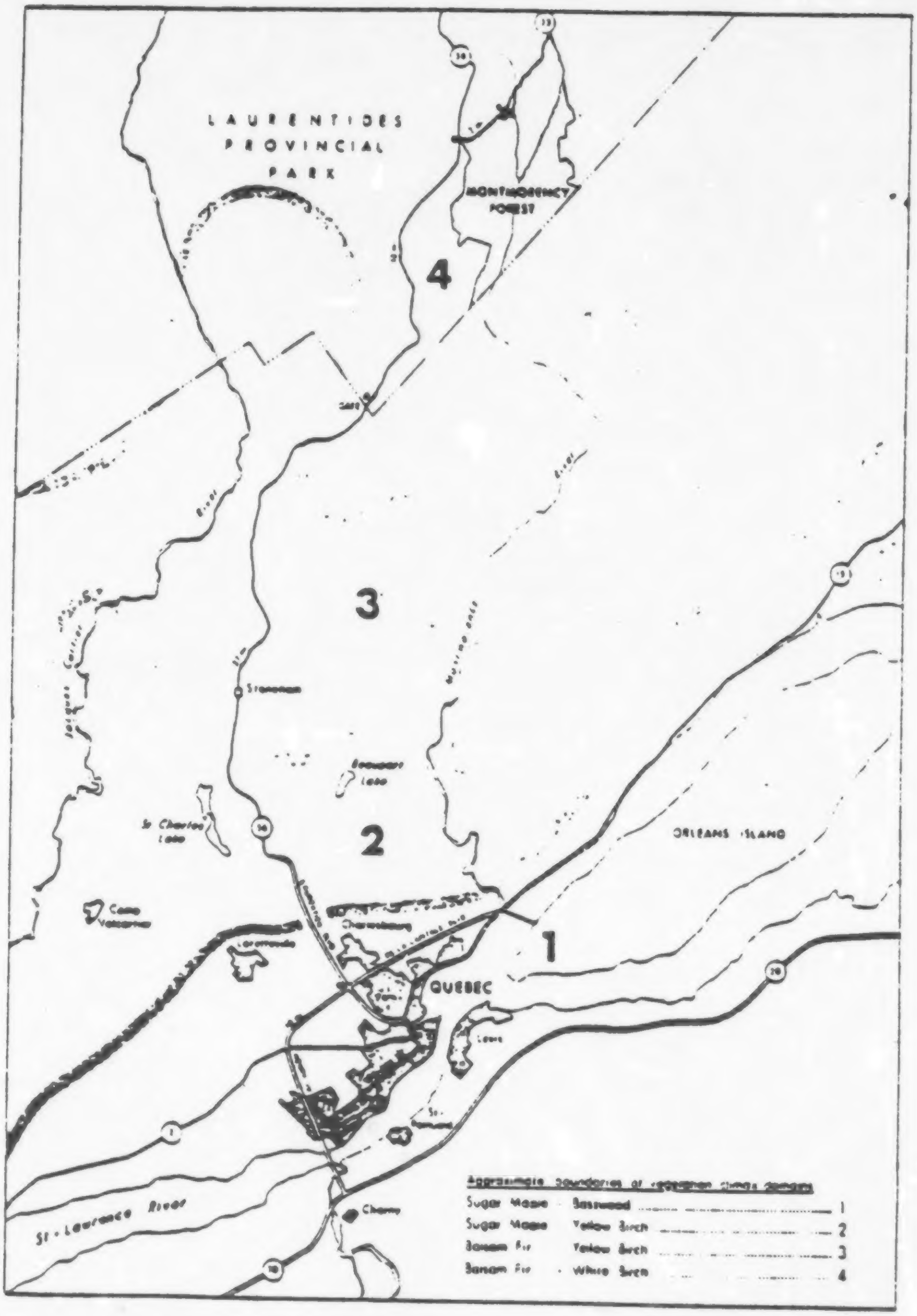
LAURENTIDES PROVINCIAL PARK
MONTMORENCY FOREST
4
3
Stoneham
Beauport Lake
St Charles Lake
2
ORLEANS ISLAND
Charlesbourg
QUEBEC
1
Levis
Charny
St-Lawrence River
Approximate boundaries of vegetation climax domains
Sugar Maple - Basswood 1
Sugar Maple - Yellow Birch 2
Balsam Fir - Yellow Birch 3
Balsam Fir - White Birch 4

Figure 1

Associated herbs: the acidophilous species *Oxalis montana, Clintonia borealis, Maianthemum canadense, Lycopodium obscurum, Lineaea borealis.* Particularities: a zone of forests and wildlife, the herbaceous layer dominated by *Oxalis montana*, and a moss layer of *Pleurozium schreberi, Hylocomnium splendens* and *Dicranum* spp. This zone includes the Lake Laflamme catchment.

North of Montmorency Forest is found the balsam fir-black spruce zone on humo-ferric podzol. Areas of alpine tundra occupy the higher summits.

Facts of interest on Montmorency Forest

Montmorency Forest is a 66 km^2 tract of land and part of the 200,000 km^2 boreal balsam fir forest which stretches across Québec from west to east.

Until the early forties it was managed, as the rest of the Laurentide Reserve, by pulpwood companies cutting the oldest classes of trees.

In 1963 the Québec government granted by law the Montmorency Forest to Laval University for a period of 99 years. The forest is administered by the university under a multiple-use management plan for education and research. A resident forest engineer with a team of 16 employees insure year-round operation of the center, which includes a residence for 150 persons with dining and recreational facilities, classrooms, office and laboratory space.

The main activities deal with: 1) forest management, which requires logging operations to remove the allowable cut. This production has been sold as pulpwood to pulp and paper mills in the Québec region; 2) education, for forestry students at Laval University undertaking field training. Primary school students also participate in an educational program for forest conservation; 3) research, undertaken by professors and students from many universities and by government agencies both federal and provincial. Research is diversified, with projects in fertilization, hydrology, climatology in relation to spruce budworm, energy from biomass and acid rain.

ENVIRONMENT RELATED TO THE LAKE LAFLAMME CATCHMENT

Climate

The climate of the area is characterized by low temperatures and abundant precipitation. It is the coldest and wettest climate of Québec province south of the 50th parallel of latitude. According to Koppen it can be classified as humid cold temperate without a dry season and with cool short summers.

Based on the data from the main weather station at the Montmorency Forest for the period 1966-1982 (Table 1, Fig. 2), the mean annual temperature was 0.2°C; the mean temperatures for the coldest (January) and warmest (July) months were -15.7°C and 14.8°C respectively. The absolute minimum was -41.0°C and the absolute maximum was 34.0°C. The mean annual number of days with frost was 233.1. Annual precipitation averaged 1,424.4 mm and ranged from 1,157.2 mm in 1968 to 1,680.2 mm in 1976. Approximately 33% of the precipitation fell as snow. The maximum precipitation for one day was 100.1 mm (11 February 1981). Snow begins to accumulate in October and disappears in May or June under forest cover. There were on an annual average 216.1 days of precipitation for this period.

Table 1. Monthly averages of several climatological parameters for the period 1968-1982 (Montmorency Forest)*

Month	Temp °C	maximum		minimum		Precipitation total mm	Rain mm	Snow mm	H.Snow cm	No. of days with pptn.
		mean °C	absolute °C	mean °C	absolute °C					
Jan	-15.7	-9.7	7.5	-21.8	-40.5	95.2	15.0	80.2	115.8	19.9
Feb	-14.4	-8.0	11.5	-20.8	-41.0	83.1	14.0	69.1	91.7	17.6
March	-7.9	-1.5	15.5	-14.4	-37.0	102.3	26.8	75.5	102.9	19.0
April	-1.2	4.6	19.0	-7.1	-28.0	87.2	43.3	43.9	59.0	15.1
May	6.3	13.0	29.0	-0.5	-17.5	100.2	90.6	9.6	10.9	14.2
June	12.3	18.9	29.5	5.7	-6.0	130.0	129.0	0.1	0.1	16.8
July	14.8	21.2	29.5	8.3	-2.5	146.7	146.7	< T	< T	17.1
August	13.4	19.3	34.0	7.4	-2.0	162.2	162.2	0.1	0.1	18.5
Sept	8.7	14.0	28.5	3.2	-10.0	138.3	136.0	2.4	2.4	17.9
Oct	2.7	7.1	24.5	-1.8	-21.0	124.9	98.2	26.7	26.3	18.4
Nov	-4.0	0.1	14.5	-8.1	-30.0	119.6	56.7	62.9	84.4	20.3
Dec	-12.1	-6.6	9.5	-18.8	-37.0	134.6	33.1	101.5	130.9	21.4
Annual values 17 yr	0.2	6.0	34.0	-5.6	-41.0	1 424.4	952.5	471.9	624.4	216.1

*Values supplied by Dr. Naud, Laval University

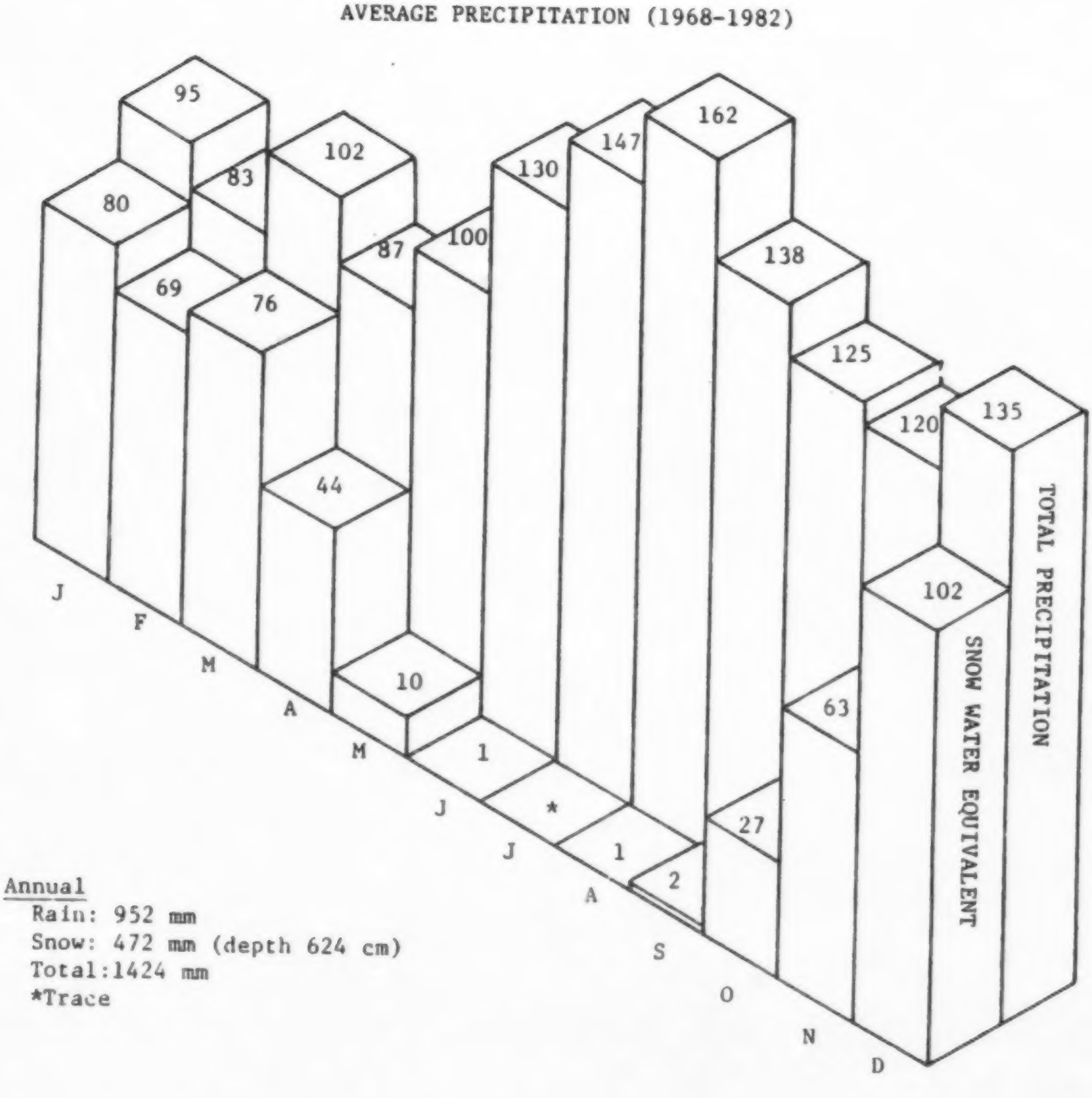
AVERAGE PRECIPITATION (1968-1982)
95
80
83
102
69
76
87
100
130
147
162
138
125
120
135
44
10
1
*
1
2
27
63
102
J
F
M
A
M
J
J
A
S
O
N
D
SNOW WATER EQUIVALENT
TOTAL PRECIPITATION
Annual
Rain: 952 mm
Snow: 472 mm (depth 624 cm)
Total:1424 mm
*Trace

Figure 2

Forest growth occurs from mid May to the beginning of October with an annual average of 143.8 days. There were on the average 1,757.2 hours of insolation per year with an evaporation of 383.2 mm for the months of June to September for the period 1967 to 1982.

As a compliment to the main weather station there are at the present 16 secondary stations that measure precipitation from June to October. Temperature and air humidity are measured at four of these stations. In winter snowfall is measured at two of these, as are snow lines. The data from these secondary stations indicate that there is a 1.08 ratio between the wettest and the driest station within the limits of Montmorency Forest. This figure suggests that the forest as a whole is wetter than indicated by the readings at the main station.

Geology and surficial deposits

The catchment lies within the Laurentian Uplands of the Canadian Shield and its formations belong to the Grenville Province. It lies entirely within a very large massif of charnokitic rocks associated with anorthosite. The charnokitic rocks vary in composition from granite to gabbro but mangerite is the more common. This rock is generally massive and porphyritic and often exhibits gneissic structures.

Ground morain of variable depth covers the area. The till is composed of boulders and cobbles in a sandy matrix. It is the predominant material and covers most of the basin except on the NE and SE elevations. The till was deposited during the Pleistocene glaciation (Fig. 3). The thickness of the till is variable. On the average it is 15 m thick under the lake and the discharge stream and decreases in depth with altitude to about 0.1 m (Fig. 4).

Vegetation*

The vegetation of the Montmorency Forest is boreal coniferous forest of the balsam fir-white birch climax zone and includes four main associations (these associations are present to a greater or lesser extent at the Lake Laflamme catchment) (Fig. 5):

(1) The most important (BA) is formed of balsam fir, with white birch, white spruce, mountain ash and occasionally black spruce. Its potential productivity and composition of the lower vegetation vary according to topography and soil.

On the well-drained podzols of the Laurentide, Montmorency and Des Neiges series, ferns (especially *Dryopteris spinulosa*) together with other acidophilous herbs, including *Oxalis montana*, are characteristic representatives of the climax sub-association (BA.d) which reaches a potential timber production of 4.9-6.3 m^3/ha/yr on the Laurentide and Montmorency soil series.

On moderately well-drained soils of the Piché and La Foi series, the proportion of herbs decreases while mosses, especially *Hylocomium splendens*, increases (*Hylocomium* variant: BA.dh); potential timber production also reaches levels of 4.9-6.3 m^3/ha/yr.

Mosses, especially *Hylocomium*, become predominant on soil of the Swain series on the fluvioglacial deposits along streams (BA.h sub-association) and still more on imperfectly drained soils of the Colligan and Lac Rossignol series, with *Sphagnum* (variant BA.hs). In both cases, potential timber production reaches 3.5 to 4.9 m^3/ha/yr.

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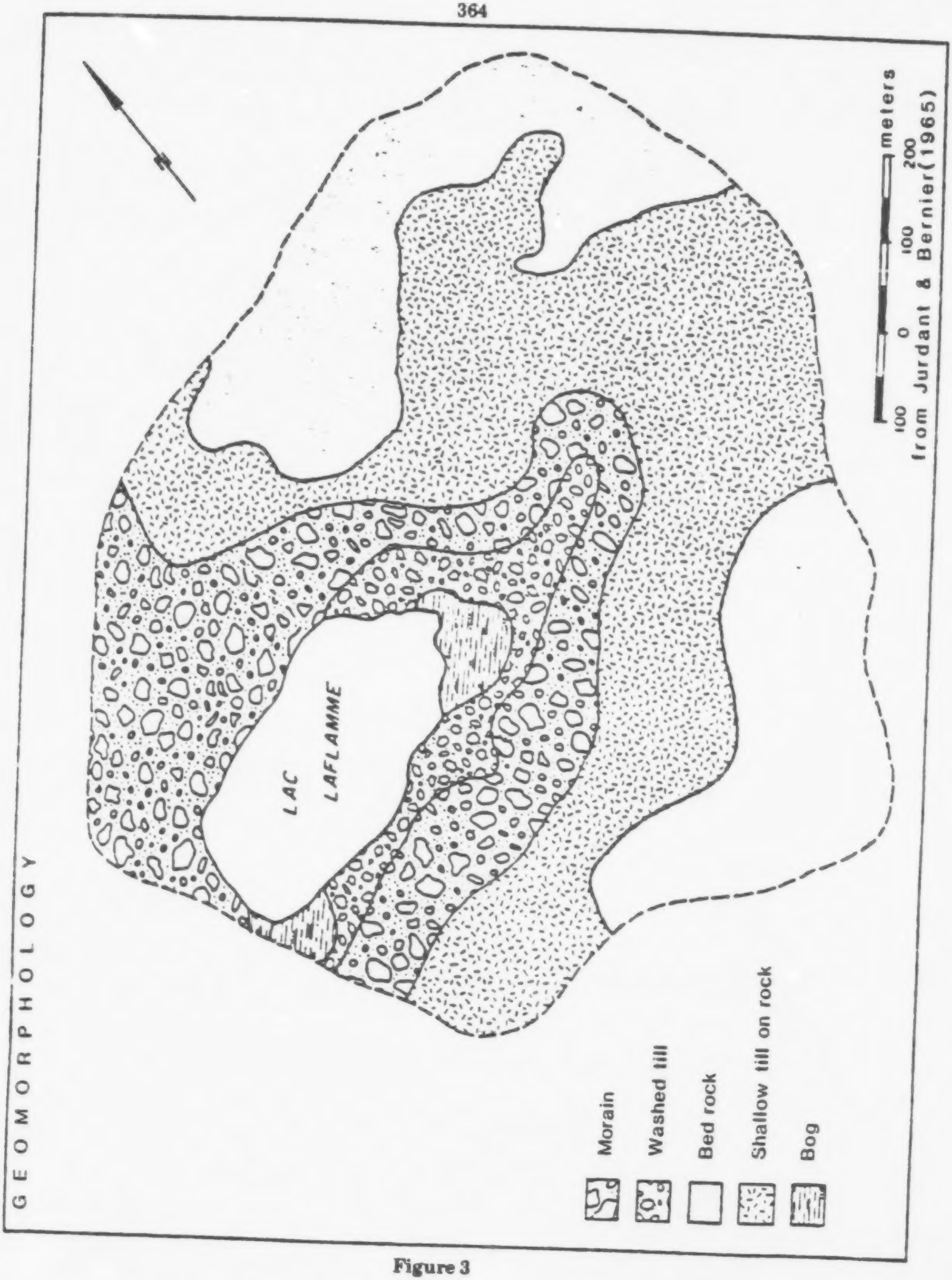
* Courtesy of Dr. M. Grandtner, Laval University



GEOMORPHOLOGY

N
LAC LAFLAMME
Morain
Washed till
Bed rock
Shallow till on rock
Bog
100
0
100
200
meters

from Jurdant & Bernier (1965)

Figure 3

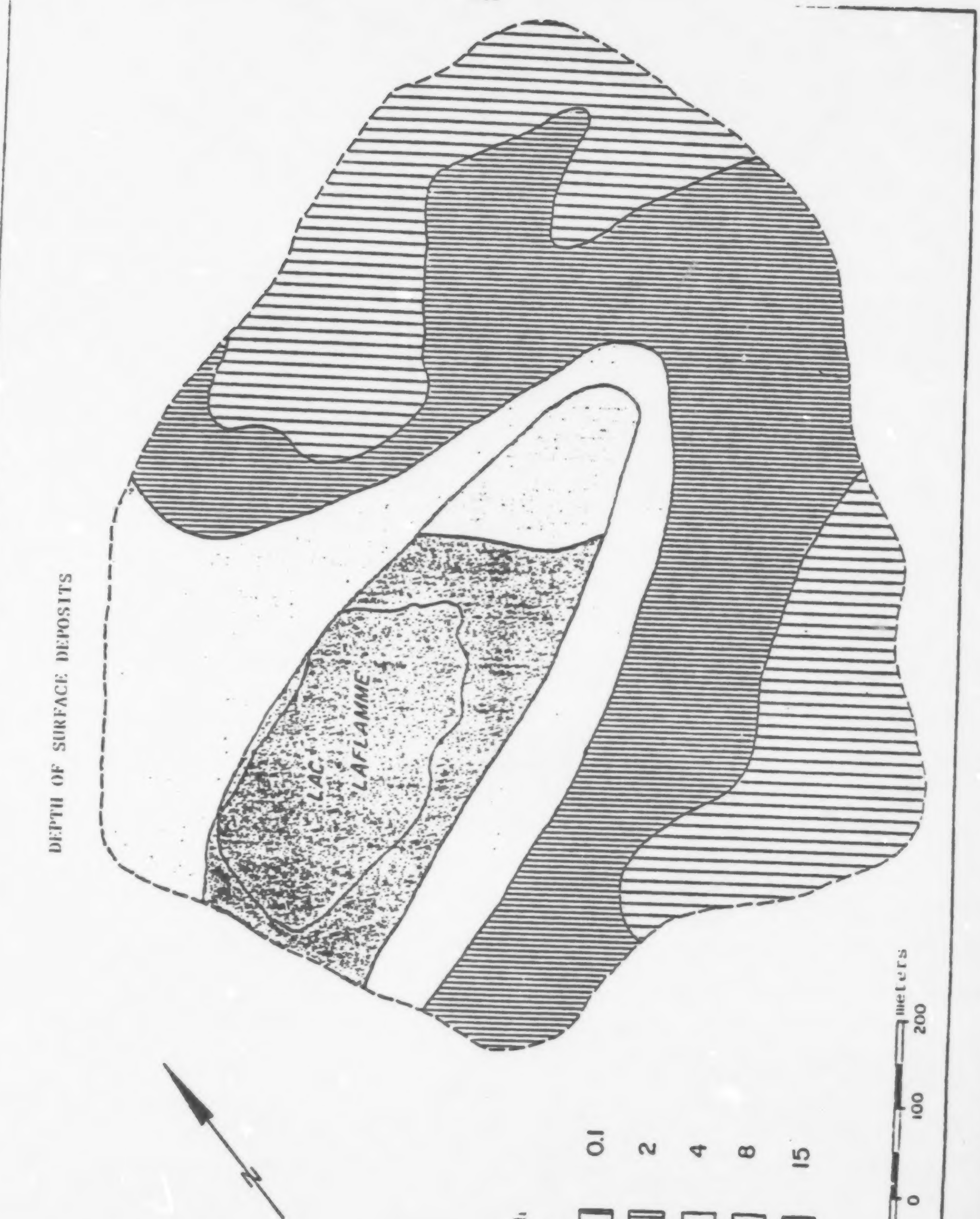
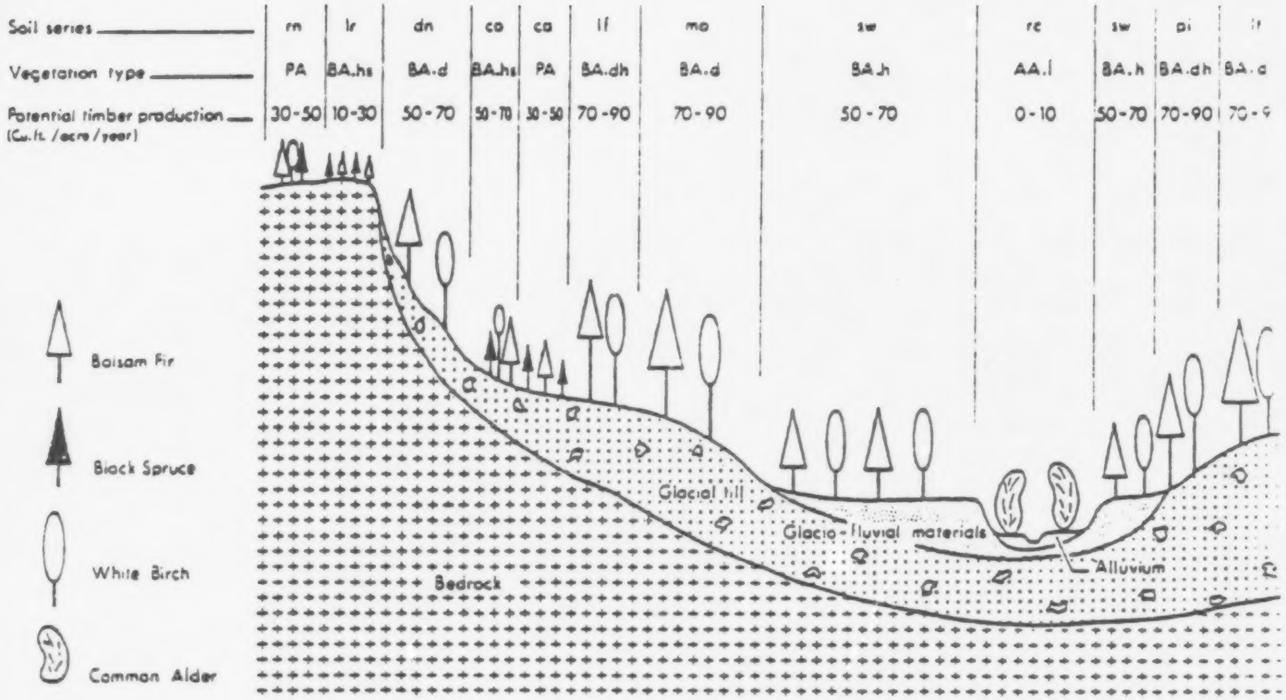

DEPTH OF SURFACE DEPOSITS
LAC LAFLAMME
N
Depth (m)
0.1
2
4
8
15
100
0
100
200
meters

Figure 4


Soil series
rn
lr
dn
co
ca
lf
mo
sw
rc
sw
pi
lt
Vegetation type
PA
BA.hs
BA.d
BA.hs
PA
BA.dh
BA.d
BA.h
AA.l
BA.h
BA.dh
BA.d
Potential timber production
(Cu.ft. /acre /year)
30-50
10-30
50-70
50-70
30-50
70-90
70-90
50-70
0-10
50-70
70-90
70-9
Balsam Fir
Black Spruce
White Birch
Common Alder
Glacial till
Glacio-fluvial materials
Alluvium
Bedrock

Soils, topography, and vegetation relationships

Soil Series Abbreviations

ca : Cauchon
co : Colligan
dn : Des Neiges
lf : La Foi
lr : Lac Rossignol
lt : Laurentide
mo : Montmorency
pi : Piché
rn : Ruisseau du Nord
rc : Rivière Cachée
sw : Swain

Legend to Vegetation Types of Montmorency Forest

Alder swamps

AA.l : Alder-balsam fir type

Balsam fir-white birch forests

BA.d : Balsam fir-white birch-*Dryopteris* type
BA.dh : Balsam fir-white birch-*Dryopteris-Hylocomium* type
BA.h : Balsam fir-white birch-*Hylocomium* type
BA.hs : Balsam fir-white birch-*Hylocomium-Sphagnum* type

Balsam fir-black spruce forests

PA : Balsam fir-black spruce type

Conversion factor 1 cu. ft./ac. equals 0.0699 m^3/ha

Figure 5

(2) On mountain summits, lithic regosols of the Ruisseau du Nord series and the imperfectly drained till of the Cauchon series support a balsam fir-black spruce forest association (PA). While balsam fir is the dominant species, white birch is very scarce and black spruce is rising in importance; mosses are numerous and abundant. The potential timber production of this forest is low (2.1-3.5 m^3/ha/yr).

(3) The wet alluvial soils of the Rivière Cachée series are colonized by the alder-club moss association (AA.1). *Alnus rugosa* v. *americana* is accompanied by a variety of mosses and hygrophilous herbs. Productivity is very low.

(4) Finally, the unproductive organic soils of the Séminaire and Lac Grand series support a bog vegetation including sparse black spruce trees.

Soils

The orthic humo-ferric podzol is the dominant soil type on the catchment. The different soil encountered on the catchment are shown in Fig. 6. The well drained soils belong to the Laurentide (it) and Des Neiges (Dn) series with the moderately drained soils belonging to the Piché (Pi) and La Foi (If) series. The gleyed humic podzols are of the Colligan series (CO) and are poorly drained. A profile description of the Laurentide soil along with some chemical characteristics are shown on the following pages (12 to 17). (Taken from the Fourth North American Forest Soils Conference. A visit to Montmorency Forest. University Laval, Quebec, 37 p.).

LAKE LAFLAMME CATCHMENT PROJECT

Location and History

The catchment is located at approximately 3 km north by road of the Montmorency Forest administration center. It is a high elevation catchment with a total surface area of 68.4 ha of which 62.3 ha is terrestrial and 6.1 ha is lake. The ratio of land/water is 10.2:1.

The site was selected in the summer of 1979. Six plots of 375 m^2 were selected in the fall of 1979 and preliminary sampling of bulk precipitation, throughfall and stemflow was initiated in one of these plots. In the summer and winter of 1980 a gauging station was established at the lake outlet and a precipitation and air quality station was established in a clearing in proximity to the lake. During this period throughfall, stemflow and soil percolate collectors were installed in the remaining five plots. Soil water samplers were also established on the lake peryphery. In 1981 and 1982 acidification studies were also started.

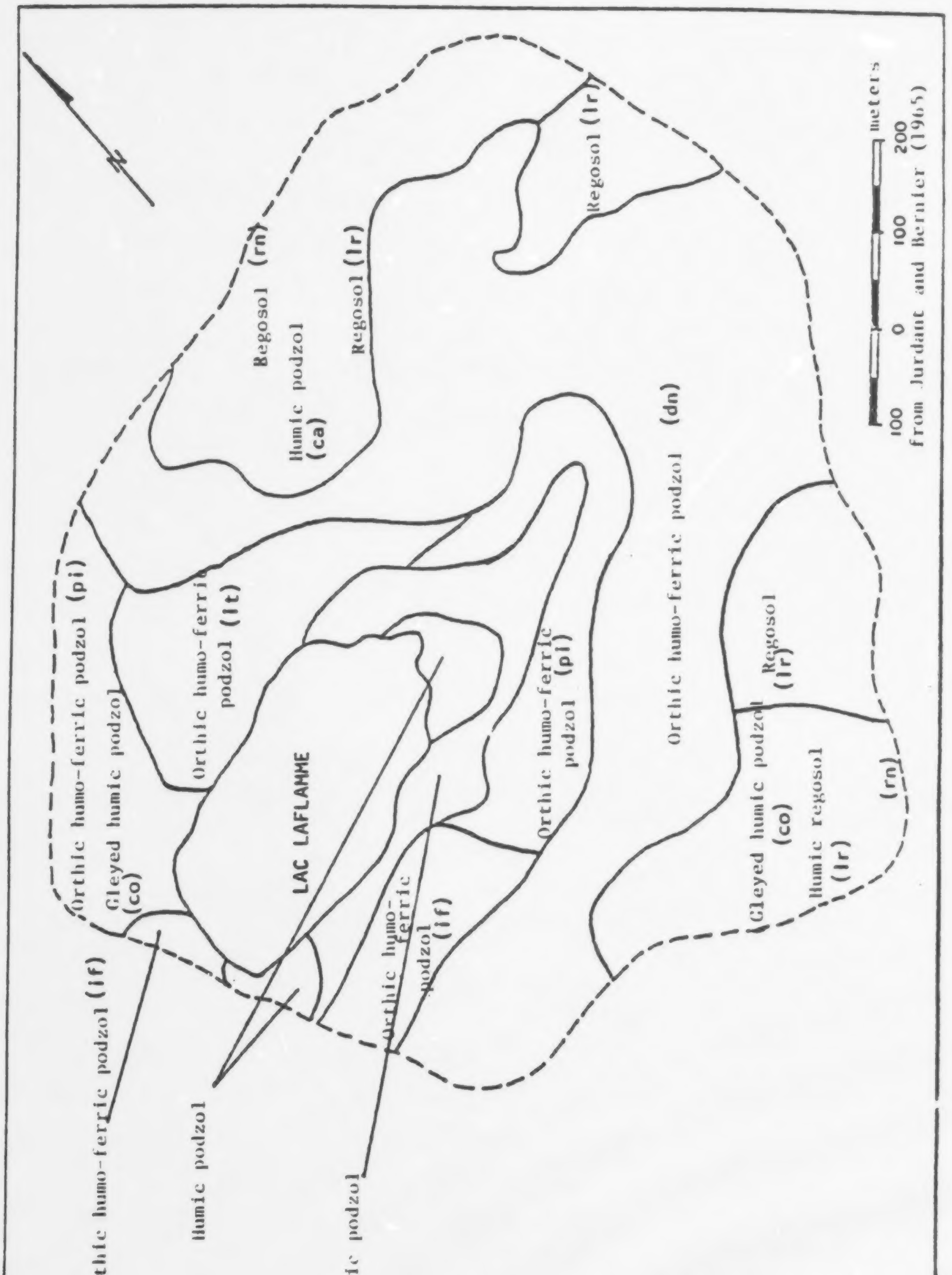
Hydrological, hydrogeochemical, climatological, vegetation, lake, ground water and snow melt chemistry, fish, phytoplancton and seismic studies were begun in 1980, 1981 and 1982.

Objectives

The objectives of the catchment approach are to:

obtain data on precipitation and air quality to estimate; the deposition and concentration of selected ions (H, Ca, Mg, K, Na, NH_4, SO_4, NO_3, PO_4 and Cl) to the terrestrial and aquatic systems; the seasonal and yearly variations in deposition and concentration.

obtain data on the changes in the quantity and chemical composition of the precipitation as it passes through the vegetation cover to estimate; the importance of dry deposition to vegetation surfaces; potential leaching of ions from the vegetation; concentrations and deposition of ions to the soil surface.


N
Regosol (rn)
Regosol
Humic podzol (ca)
Regosol (lr)
Regosol (lr)
Orthic humo-ferric podzol (dn)
Orthic humo-ferric podzol (pi)
Orthic humo-ferric podzol (lt)
Gleyed humic podzol (co)
LAC LAFLAMME
Orthic humo-ferric podzol (pi)
Orthic humo-ferric podzol (lf)
Regosol (lr)
Gleyed humic podzol (co)
Humic regosol (lr)
(rn)
Orthic humo-ferric podzol (lf)
Humic podzol
Humic podzol
100 0 100 200 meters

from Jurdant and Bernier (1965)

Figure 6

Table 2. Profile description of Laurentide soil

Horizon	Depth (cm)	Morphology
LFH	8-0	Black (10 YR 2/1 m), very dark grayish brown (10 YR 3/1 d), semi-decomposed to well-decomposed organic matter; fibrous to fine granular; abundant fine and medium roots; abrupt, smooth boundary; 5 to 15 cm thick; pH 3.6
Ae	0-5	Gray (7.5 YR 5/0 m), light gray (7.5 YR 7/0 d) loamy sand; single grain to weak fine subangular; firm in place, friable when removed; few fine and medium roots; abrupt, wavy to irregular boundary; 3 to 13 cm thick; pH 3.9
Bhf_1	5-11	Very dark reddish brown (5 YR 2/2 m), dark brown (7.5 YR 3/2 d) sandy loam; weak fine granular to weak medium granular, breaks into soft peds; firm in place, friable when removed; few fine and medium roots; abrupt wavy boundary; 2 to 12 cm thick; pH 3.9
Bhf_2	11-17	Dark reddish brown (2.5 YR 2/4 - 5 YR 3/2 m), brown (7.5 YR 4/4 d) sandy loam; weak very fine to weak medium granular, breaks into soft peds; firm in place, very friable when removed; few fine to medium roots; clear wavy boundary; 3 to 7 cm thick; pH 4.4
Bfh	17-27	Dark brown to dark reddish brown (7.5 YR 4/4 - 5 YR 4/4 m), yellowish brown (10 YR 5/4 d) loamy sand; compound weak fine to medium granular and weak fine subangular blocky; firm in place, friable when removed; very few fine roots; clear smooth boundary; 7 to 12 cm thick; pH 4.6
Bf	27-40	Dark yellowish brown (10 YR 4/4 m), light yellowish brown (10 YR 6/4 d) sandy loam; weak fine to medium subangular blocky; firm in place, friable when removed; gradual smooth boundary; 10 to 15 cm thick; pH 4.7
BC	40-56	Olive brown (2.5 Y 4/4 m), light yellowish brown (2.5 Y 6/4 d) loamy sand; compound weak fine to medium subangular blocky and moderate medium platy; firm in place, friable when removed; gradual smooth boundary; pH 5.0
Cx	56-	Olive to dark olive (5 Y 4/3 - 5 Y 3/3 m; 5 Y 5/3 d) loamy sand; moderate coarse platy; very firm in place, friable when removed, brittle, reaches maximum consistence between 150 and 250 cm; some stones; pH 5.0

Table 3. Particle size distribution of the Laurentide soil

		Sand %						Silt %				Clay %		
Horizon	Depth (cm)	Very coarse 2.0-1.0 mm	Coarse 1.0-0.5 mm	Medium 0.5-0.25 mm	Fine 0.25-0.1 mm	Very fine 0.1-0.05 mm	TOTAL 2-0.05 mm	Coarse 50-20 µm	Medium 20-5 µm	Fine 5-2 µm	TOTAL 50-2 µm	Coarse 2-1 µm	Medium + Fine < 1 µm	TOTAL < 2µm
Ae	0-5	7.9	12.8	13.2	28.6	16.2	78.6	10.9	7.3	1.6	19.8	0.6	1.0	1.6
Bhf_1	5-11	7.0	13.1	13.5	24.0	14.2	71.8	11.8	7.3	1.9	21.0	1.3	5.9	7.2
Bhf_2	11-17	7.7	12.3	13.2	24.2	14.6	72.1	10.1	6.4	2.4	18.9	2.1	6.9	9.0
Bfh	17-27	9.3	14.9	12.7	23.8	17.3	78.0	9.4	5.9	1.3	16.6	0.2	5.2	5.4
Bf	27-40	8.7	14.4	11.2	19.9	13.8	67.9	14.8	9.8	2.9	27.5	1.4	3.2	4.6
BC	40-56	4.6	10.9	10.7	25.2	19.7	71.1	16.9	8.2	2.2	27.3	0.9	0.7	1.6
Cx_1	56-120	7.5	13.9	12.6	26.9	19.2	80.1	13.4	3.6	1.4	18.4	0.7	0.8	1.5
Cx_2*	120-150	9.1	12.7	11.8	26.3	17.2	77.1	13.1	6.6	1.4	21.1	0.7	1.1	1.8
Cx_3*	150-240	8.4	12.1	12.3	27.9	18.1	77.8	13.3	6.0	0.9	20.2	0.2	0.8	1.0
Cx_4*	240-330	8.8	12.3	12.2	26.8	17.4	77.5	10.7	8.8	1.4	20.9	0.8	0.8	1.6

*Sampled about 400 ft. distant from the original pit

Analysis done under the direction of G. Bourbeau

Table 4. Organic matter, free and total Fe and Al in the Laurentide soil

Horizon	Depth (cm)	Organic matter %	Fe.ox %	Al.ox %	Fe.di %	Al.di %	Fe.py %	Al.py %	Fe.t %	Al.t %	Δ(Fe + Al).ox (B - C)	O.M. / Fe.ox	Fe.ox / Fe.di	(Fe + Al)py / (Fe + Al)di	Fe.t- / Fe.d	Al.t- / Al.di	Fe.di / Clay	(Fe + Al)py / Clay
Ae	0-5	1.15	0.05	0.02	0.02	0.02	0.02	0.02	4.27	6.03		23.0	2.5	1.0	4.85	6.01	0.01	0.02
Bhf$_1$	5-11	15.70	3.63	1.14	3.53	1.42	3.31	1.50	6.78	5.39	3.79	4.3	1.03	0.97	3.25	3.97	0.49	0.67
Bhf^2	11-17	13.77	2.75	2.79	2.95	3.53	2.36	3.39	6.36	7.20	4.56	5.0	0.93	0.89	3.41	3.67	0.33	0.64
Bfh	17-27	6.55	1.87	2.40	2.12	3.01	1.48	2.83	5.62	7.76	3.29	3.5	0.88	0.84	3.50	4.75	0.39	0.80
Bf	27-40	2.77	1.02	1.51	1.24	1.58	0.56	0.94	5.17	7.56	1.55	2.7	0.82	0.53	3.93	5.98	0.30	0.33
BC	40-56	1.00	0.57	0.97	0.77	0.63	0.17	0.58	4.94	7.56	0.56	1.7	0.74	0.53	4.17	6.93	0.48	0.47
Cx$_1$	56-120	0.94	0.45	0.53	0.54	0.32	0.03	0.22	5.26	7.17		2.1	0.83	0.29	4.72	6.75	0.36	0.17

Analysis done by A. Gonzalez

Table 5. Some chemical characteristics of the Laurentide soil

Horizon	pH $CaCl_2$ 0.01 M	Ca meq/100g	Mg meq/100g	Al meq/100g	Eff.CEC meq/100g (1)	% Base saturation (2)	pH-7 CEC meq/100g (3)	Inorganic pH-7 CEC meq/100g (4)	Δ CEC meq/100g (5)	$\frac{\Delta \text{CEC}}{\text{Eff. CEC}}$
Ae	3.5	1.19	0.01	1.25	2.45	49.0	3.0	1.5	0.55	0.22
Bhf_1	3.6	14.12	0.02	18.90	33.04	42.8	51.2	12.5	18.16	0.55
Bhf_2	4.1	8.75	0.01	8.05	16.81	52.1	36.0	10.5	19.20	1.14
Bfh	4.2	2.45	0.01	3.74	6.20	39.7	23.8	14.0	17.60	2.84
Bf	4.3	1.51	0.01	2.22	3.74	40.6	14.1	4.5	10.36	2.77
BC	4.3	0.97	0.01	1.39	2.37	41.3	8.5	7.5	6.13	2.59
Cx_1	4.7	0.45	0.01	0.83	1.29	35.6	4.0	4.0	2.71	2.10

(1) Effective CEC = Σ (Ca + Mg + Al) 2N NaCl extract

(2) (Ca + Mg) / (Ca + Mg + Al), 2N NaCl extract

(3) {Ca $(OAc)_2$ + $CaCl_2$} extract

(4) As (3), but organic matter removed

(5) Δ CEC = pH-dep.CEC = (ph-7 CEC - eff.CEC)

Analysis done by Y. Laflamme

Table 6. Additional chemical characteristics of the Laurentide soil

Horizon	Nt	Avail.P	CEC	Exch. cations		(2)
	(%)	ppm (1)	meq/100g (2)	Ca	Mg (meq/100g)	K
LF	1.59	185	91.2	8.12	2.30	2.02
H	1.53	125	73.0	6.00	1.98	1.24
Ae	0.05	11	2.8	0.36	0.16	0.11
Bhf_1	0.50	36	108.0	0.51	0.27	0.21
Bhf_2	0.36	120	78.0	0.47	0.14	0.11
Bfh	0.22	74	49.7	0.50	0.12	0.06
Bf	0.12	38	31.0	0.55	0.12	0.06
BC	0.06	21	16.8	0.55	0.14	0.08
Cx_1	0.02	17	9.0	0.57	0.13	0.09

(1) Olsen's method

(2) pH-7 NH_4OAC

Table 7. Mineralogical composition of fine sand fraction of the Laurentide soil *

	Horizon						
	Ae	Bhf$_1$	Bhf$_2$	Bfh	Bf	BC	Cx$_1$
Light minerals (s.g. < 2.96)	82	79	81	86	82	80	79
Quartz	59	54	46	45	52	53	43
Feldspars	23	25	35	41	30	27	36
Heavy minerals (s.g. > 2.96)	18	21	19	14	18	20	21
Magnetite-Ilmenite	9	9	6	5	9	8	8
Hypersthene	4	5	4	2	3	3	4
Hornblende	2	3	3	3	4	4	4
Augite	2	3	3	2	2	2	2
Others	1	1	3	2	< 1	3	3

*expressed as % by weight, free iron-oxides and organic matter removed Mineralogical analysis done by R. Ledoux and J. Trencia

Table 8. Concentrations (μeq L-1) of major ions for various components of the water cycle in the Lake Laflamme catchment

Ions	Bulk[1] precipitation μeq L-1	Throughfall[1] μeq L-1	Stemflow[1] μeq L-1	Soil[1] percolate μeq L-1	Lake[2] μeq L-1	Lake[2] outlet μeq L-1
H	39.8 (4.40)[3]	39.8 (4.40)	72.4 (4.14)	13.5 (4.87)	0.6 (6.30)	0.8 (6.10)
K	0.7	19.8	148.5	7.1	5.4	5.1
Ca	6.9	24.9	113.8	122.4	129.7	119.8
Mg	1.7	10.7	37.7	28.7	44.4	41.1
Na	10.5	13.0	16.2	30.9	43.5	43.5
NH_4	trace	trace	2.0	0.4	-	-
PO_4	1.0	7.8	133.5	0.1	0.01	0.01
SO_4	52.2	73.6	198.4	111.3	77.0	79.0
Cl	13.5	17.4	24.6	21.3	11.3	14.1
NO_3	7.3	0.2	1.5	171.2	10.0	10.0

[1] June to October 1982

[2] January to December 1982

[3] ( ) pH values

obtain data on the chemistry of soil percolates to estimate; the potential leaching of the major ions and the potential inputs to the aquatic system.

obtain data on the quantity and quality of snowmelt to estimate; potential inputs of ions to the organic layer and mineral soil and to the aquatic system; the effect on the acid shock.

obtain data on the snow chemistry in the open and under forest cover to estimate; winter inputs of ions to the catchment; contribution to acid shock.

obtain data on lake chemistry to estimate; potential contributions of ions to acid shock; potential effects on the aquatic life; potential alteration in lake chemistry in the long term.

obtain data on the chemistry of the lake water inputs and outputs to estimate; the potential for the net exportation of ions from the catchment.

to estimate the flux of ions through the catchment.

to estimate the potential effects of acidification on the accumulation of bioelements by the vegetation; the effects on organic matter; the effects on micro-organisms and the potential effects on the development and function of mycorrhizi.

Excursion stops

Stop One: Inputs to the catchment

The inputs of the major ions to the catchment are estimated from precipitation samples (rain, snow, hail etc.) collected from a Sangamo wet precipitation only collector and from open 'bulk' samplers. Inputs from aerosols and particulates are estimated from samples taken from filter packs placed on a 10 m boom. The quantity of precipitation is taken from a standard rain gauge, while duration and intensity of the precipitation are taken from a registering standard tipping bucket gauge. Precipitation samples are usually collected at 8h00 every day and aerosols and particulates are sampled continuously for 24 hrs. The average seasonal volume weighted concentrations for samples taken from bulk collectors are given in Table 2.

Stop Two: Aquatic system

Studies on the ionic budget, vegetation, fish and phytoplancton have been in progress since 1980 under the supervision of the Inland Waters Directorate, Québec Region. Associated with these studies is one characterizing the spring acid shock which takes into account the ionic fluxes from snowmelt water.

The ionic matrix of the water is dominated by Ca, HCO_3 and SO_4. The lake is slightly acid (pH 6.1) and is responsive to acid input as revealed by the acid shock study. The ionic budget has been calculated for 1981. It indicates that Ca, Mg, Na, K, SO_4, Cl and HCO_3 are exported from the catchment and that H and NO_3 are retained. Table 2 shows typical values of ion concentrations for 1982.

Stop Three: Canopy influence

The concentration matrix of the incident precipitation changes dramatically on contact with the canopy. This change may be a result of dry deposition, the giometry of the canopy (density, volume, frequency), the leaching of ions by an ion exchange mechanism, evapotranspiration and the type of canopy intercepting the precipitation (coniferous vs deciduous, species differences).

It is important to determine this new concentration matrix on a seasonal basis. Primarily we want estimates of the concentration and deposition that impinges the organic layer to help us evaluate indirect effects to nutrient availability as well as contributions to the aquatic system via spring melt for example

At this stop you will see one of the six plots established on the catchment to evaluate the matrix change. It is a 375 m^2 plot instrumented with throughfall and stemflow collectors as well as soil percolate lysimeters. Typical values are given in Table 2. There is an enrichment of all ions except NO_3. It should be noted that the quantity of throughfall and stemflow represent 33 and 2% respectively of the incident precipitation.

Stop Four: Hydrology and climatology

These studies are done jointly by the Inland Waters Directorate, the Canadian Forestry Service and Laval University. The hydrometeorological and climatological studies started in 1980.

The quantitative estimate of the water flux through the catchment is necessary to interprate temporal and spatial changes in the ionic fluxes. The parameters quantified are precipitation, interception, infiltration, evapotranspiration, runoff, storage, temperature, insolation and thermal flux. To quantify spring melt a 20 m^2 surface lysimeter and a pit lysimeter that collected water flowing parallel to the slope were installed.

From June 81 to May 82 the monthly precipitation ranged from 35 to 200 mm for a total of 1,183 mm which was less than what was registered at the main weather station (1,429 mm). The average air temperature, for periods of 10 days varied from 18°C (July) to - 24°C (January). At a 10 cm depth in the soil the temperature reached a maximum of 12°C (July and September). For the period from December to mid May soil temperature was approximately -1°C.

The flow rate at the output stream ranged from 0.01 to 0.04 m^3/s during the summer months and responded rapidly to precipitation events. A maximum of 0.95 m^3/s was obtained on May 9, 1982 and corresponded to maximum snowmelt accompanied by a rain event.

Rain interception was studied in stands of different ages, stem height and cover. interception ranges from 38 to 15% and is a function of precipitation type and cover closure. The average interception for the catchment was 33%. The loss by evapotranspiration was 40% of the annual precipitation.

Stop Five: In situ acidification

Both the Laurentian and Great Lakes Forest Research Centers have initiated acidification studies in the catchment. These studies will give some insight to the biological and root-soil effects of acidification.

One study under the direction of researchers from Queen's University in Kingston, Ontario, looked at the effects on fungi and bacteria and the possible reprecussions on the S and N cycle. A second, under the responsibility of researchers from Laval University, Ste- Foy, Québec, will look at the effects on the development and function of myccorhiza associated with balsam fir and white birch. A third study, which you will see, estimates chemical changes in the organic layer and top 10 cm of inorganic soil and the bio-element accumulation by *Oxalis montana* in both below and above ground parts.

Stop Six: Outputs from the catchment

A Parshall flume was established in 1980 to monitor the outlet water volume. Water samples are taken to estimate the concentrations and fluxes of ions from the catchment. Table 2 gives some typical concentrations from January to December 1982.

AGENCIES PARTICIPATING IN THE LAKE LAFLAMME PROJECT

Envirnoment Canada
Canadian Forestry Service
Laurentian Forest Research Center, Ste-Foy, Québec
Great Lakes Forest Research Center, Sault Ste Marie, Ontario
Inland Waters Directorate, Québec Region, Ste-Foy & Longueuil, Québec
Lands Directorate, Québec Region, Ste-Foy, Québec

Ministry of Fish and Oceans, Québec Region

Laval University, Ste-Foy, Québec
Forestry and Geodesy Dept.
Geology Dept.
Biology Dept.
Queen's University, Kingston, Ontario
Geography Dept.
Chemistry Dept.
Microbiology Dept.

INRS-Eau, Ste-Foy, Québec

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POSTER PAPERS

Modelling and Verifying the Effects of Acid Precipitation on Soil Leachates

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ABSTRACT

A model for predicting the effects of acid precipitation on the acid ($H^+ + Al^{3+} + Fe^{3+}$) and base ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$) cation losses from soils through leaching as a function of time was verified by examining published results for one indoor and five outdoor lysimeter studies (with precipitation pH values ranging from 2 to 6) and five watershed studies. In each case the predictions of the model were in acceptable agreement with the observed acid and base cation losses. These studies were selected from other relevant studies because they nearly met the information requirements of the model. The prediction of the acidic cation content of soil leachates is important for considering the generally negative effects of such cations (especially the dominating Al^{3+} ions) on plant growth and ground, stream and lake water quality. Details regarding the model and its verification can be found in: Ecological Modelling, 19:105-138 (1983) and also in: Canadian Hydrology Symposium 1982 (Fredericton, NB):615-635.

Analysis of Percolates From an Acidified (H_2SO_4) Humo-Ferric Podzol

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Organic horizons (LF and H), as well as organic-spodic horizons (LF, H, Ae, Bhf_1 and Bhf_2), were reconstituted in 10-cm plastic columns. The humo-ferric podzol (Laurentide series) tested came from the Lake Laflamme catchment (Montmorency Forest), located 80 km north of Québec City. The soil columns (three replicates) were leached for 24 weeks with acidified water at the following concentrations: 1250 (pH 2.9), 500 (pH 3.3), 50 (pH 4.3) and 0 (pH 5.6) µeq L^{-1} of H at a rate of 6.2 cm wk^{-1}.

Preliminary results indicate that 80% of the total ionic charge of the percolates from the organic horizons came from the SO_4, NO_3, NH_4 and Ca ions. All of the SO_4 ions are leached. An excess of 130 ± 30 µeq L^{-1} of SO_4 was found, presumably as a result of mineralization. Inorganic N is constant in all percolates from all of the treatments, but the relative contribution of NO_3 increased by 28% at pH 2.9 to 50% at pH 5.6. The leaching of Ca (>100%), Mn (>100%) and Mg (>50%) in the pH 2.9 treatment is significant compared with the control (pH 5.6).

On the other hand, 90% of the total ionic charge of the percolates from the organic-spodic horizons was composed, in decreasing order, of NO_3, Al, Ca and SO_4 ions. Forty-seven percent and 38% of the SO_4 ions originating from the organic horizons were retained for the pH 2.9 and pH 5.6 treatments respectively. This was probably due to absorption by Fe and Al sesquioxides. There was no significant difference in NO_3 content from one treatment to the next. However, there was a significant increase in the concentration of NH_4 between treatments at pH 2 9 and pH 5.6. Aluminum was found in significant concentrations at pH 2.9 only during the last 12 weeks of the leaching experiment. Concentrations of Ca, Mn and Mg increased significantly in the pH 2 9 treatment by 38%, 250% and 40% respectively when compared to the control. All of the PO_4 (160 µeq L^{-1}) coming from the organic horizons was retained by the spodic horizons.

Effects of Acid Deposition on Soil and Litter Properties: Lysimeter and Field Studies

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INTRODUCTION

A major effect of acid deposition on litter and soil is claimed to be accelerated leaching of basic cations (Ca^{2+}, Mg^{2+}, K^+) from cation-exchange sites and their replacement by H^+. The mobilization of Al also increases, as in mineral soils of pH 3.5 to 5.5 solution and precipitation of Al are the main buffering mechanisms (Bache 1980). The effects of acid deposition on soil biological processes have recently been reviewed (Andersson et al. 1981). Some studies claim to have detected effects, whereas others have found no effect on the same processes (Andersson et al. 1981). This may be because treatments were applied for too short a duration or at too high a concentration. This paper reports an outline of some of the results of a long-term study in which a soil was watered at a reasonably realistic pH (Rippon 1980). These results are compared with those found in a similar forest soil in the field, in order to highlight similarities and differences compared to the laboratory study.

METHODS

Lysimeter Cores

Cores of undisturbed soil (0.8 m diameter x 1.35 m deep) were taken in fibreglass cylinders from an area of mixed coniferous-deciduous woodland. The soil and vegetation collection and watering methods have been described elsewhere (Rippon 1980). Pairs of lysimeters received either distilled water or sulphuric acid (pH 3) at about 1500 mm yr^{-1} for almost 5 years. At the end of the experiment, the organic material comprising litter and humus (henceforth called 'litter') was separated from the underlying mineral soil and homogenized. The mineral soil was removed in successive 3-cm-thick increments. Standard methods, to be referred to in later publications, were used to measure the properties of the <2-mm fraction of the soil.

Field Studies

Bulk precipitation and throughfall were collected by standard methods as described in Skeffington (1981). Soil properties were measured under isolated individuals of the three tree species by sampling at three 10-cm depth intervals at three distances from the trunk and in three directions with three individuals of each species. Soil pH was measured in $CaCl_2$; subsequently an equilibrium soil solution (Ulrich et al. 1980) was prepared and the ion content measured.

RESULTS

The results in Table 1 show the effect of acid treatment on the ionic composition of litter from the lysimeters. Significant decreases in pH, base saturation, and basic cations were observed, with significant increases in extractable sulphate and aluminum.

The acidification observed in the litter layer due to acid treatment persisted in the mineral soil down to about 80 cm (Fig. 1). Most of the Ca^{2+}, Mg^{2+} and Mn^{2+} in the mineral soil occurred in the organically rich soil above 15 cm depth. The concentrations of Ca, Mg and Mn in these layers are shown in Table 2, expressed on an organic matter basis in order to remove the confounding effects of pre-existing differences in organic matter content between lysimeters, as these ions correlate well with organic matter. There was a less marked effect than in the litter, and little effect could be discerned below 15 cm.

The concentration of extractable Al was not correlated with organic matter and increased with depth in both acid-treated and control lysimeters (Fig. 2). Acid treatment appeared to decrease the availability of Al, except in the top 3 cm.

Some biochemical properties of litter were also altered by acid treatment (Table 3). ATP content is an indicator of microbial biomass in soil, and respiration reflects general metabolic activity. In addition to these changes in biochemical activity there was a small decrease (5.3%; $p < 0.05$) in the amount of litter decomposed in the acid-treated lysimeters over the duration of the experiments. In mineral soil, where ATP content alone was measured, only the top 3 cm showed a significant decrease due to acid treatment (10.7 $\mu g\ g^{-1}$ organic matter to 9.39 $\mu g\ g^{-1}$ organic matter).

Acid-treatment effects undoubtedly have occurred in these lysimeters, but the flux of H^+ applied was higher than that found under field conditions. However, under certain species of tree in areas with relatively high SO_2, deposition of H^+ and SO_4^{2-} can attain the same order of magnitude. Table 4 shows deposition under three tree species in such an area — the Tillingbourne Catchment, southern England (Skeffington 1981, 1983a). Although H^+ deposition in bulk precipitation is only 5% of that applied to the lysimeters, this figure increases to 40% under pine (*Pinus sylvestris* L.). Concentrations of H^+ and SO_4^{2-} under pine are actually higher than those applied to the acid-treated lysimeters (Table 3). If effects similar to those in the lysimeters are a reality in the field, then the soil under the tree canopy should show lower pH and contain less extractable Ca, Mg and Mn and possibly less Al compared with the soil away from the canopy. In Table 4, samples at 30 cm and 1 m from the trunk were under the canopy, whereas those at 5 m were outside. The soil pH was significantly lower under the canopy of not only pine but also oak (*Quercus robur* L.) and birch (*Betula pendula* Roth.). There was a tendency for the concentrations of Ca, Mg and Mn to be higher under the canopy, whereas Al was lower under the pine canopy but not under the other tree species (Table 5). This result shows that the soil under trees in the field behaved differently from that in vegetation-free lysimeters even though subject to similar levels of acid deposition. The soil pH is depressed, but there must be a mechanism maintaining levels of Ca, Mg and Mn under the trees. This mechanism may be nutrient cycling in throughfall and litterfall. Table 6 shows some data from a short-term study of throughfall composition, in which levels of all ions can be seen to be enhanced in throughfall in comparison to bulk precipitation. This is true even under the deciduous trees in this winter period. It was suggested elsewhere that the apparently loose cycling of Ca and Mg in throughfall and litterfall might be a mechanism which assists survival of trees on acid soils (Skeffington 1983b).

DISCUSSION

Five years of acid watering with sulphuric acid at pH 3 have undoubtedly altered the chemical and biochemical properties of the soil in the lysimeters. The question of whether this would occur in the field remains open. In the field, concentrations are generally lower, and rain always contains basic cations which alleviate the acidifying effect. In areas subject to high SO_2 levels, H^+ and SO_4^{2-} are enhanced in throughfall under the forest canopy, but then so are Ca and Mg. Trees can also recycle nutrients in litter. These effects should be taken into account when assessing the effect of acid precipitation on soil and forests.

Table 1. Effect of acid treatment on some chemical properties of litter

Property*	Controls	Acid-treated
pH(H_2O)	4.12	3.32
pH($CaCl_2$)	3.45	2.63
Base saturation, %	26	5.0
Extractable ions: **		
Ca^{2+}	11.8	1.39
K^+	0.53	0.37
Mg^{2+}	2.70	0.28
Mn^{2+}	0.32	0.02
Al^{3+}	0.33	0.69
SO_4^{2-}	0.15	0.71

* The data are the means of duplicate determinations on duplicate lysimeters. The effect of acid treatment on all the properties was significant at $p < 0.001$.

** Extractable ions were extracted with 2.5% (v/v) acetic acid solution. Units are meq 100 g^{-1} dw.

Table 2. Depth distribution of Ca^{2+}, Mg^{2+} and Mn^{2+} in surface mineral soil of control (C) and acid-treated (A) lysimeters

Depth	Ca^{2+}		Mg^{2+}		Mn^{2+}	
(cm)	C	A	C	A	C	A
0-3	13.4	6.5	2.6	0.9	0.31	0.12
3-6	11.0	6.8	2.1	1.0	0.22	0.13
6-9	7.1	6.2	1.3	0.9	0.12	0.10
9-12	8.6	6.7	1.4	1.0	0.12	0.11
12-15	8.5	7.1	1.3	0.9	0.10	0.09

The data are the means from duplicate lysimeters.
Units: meq 100 g^{-1} organic matter.

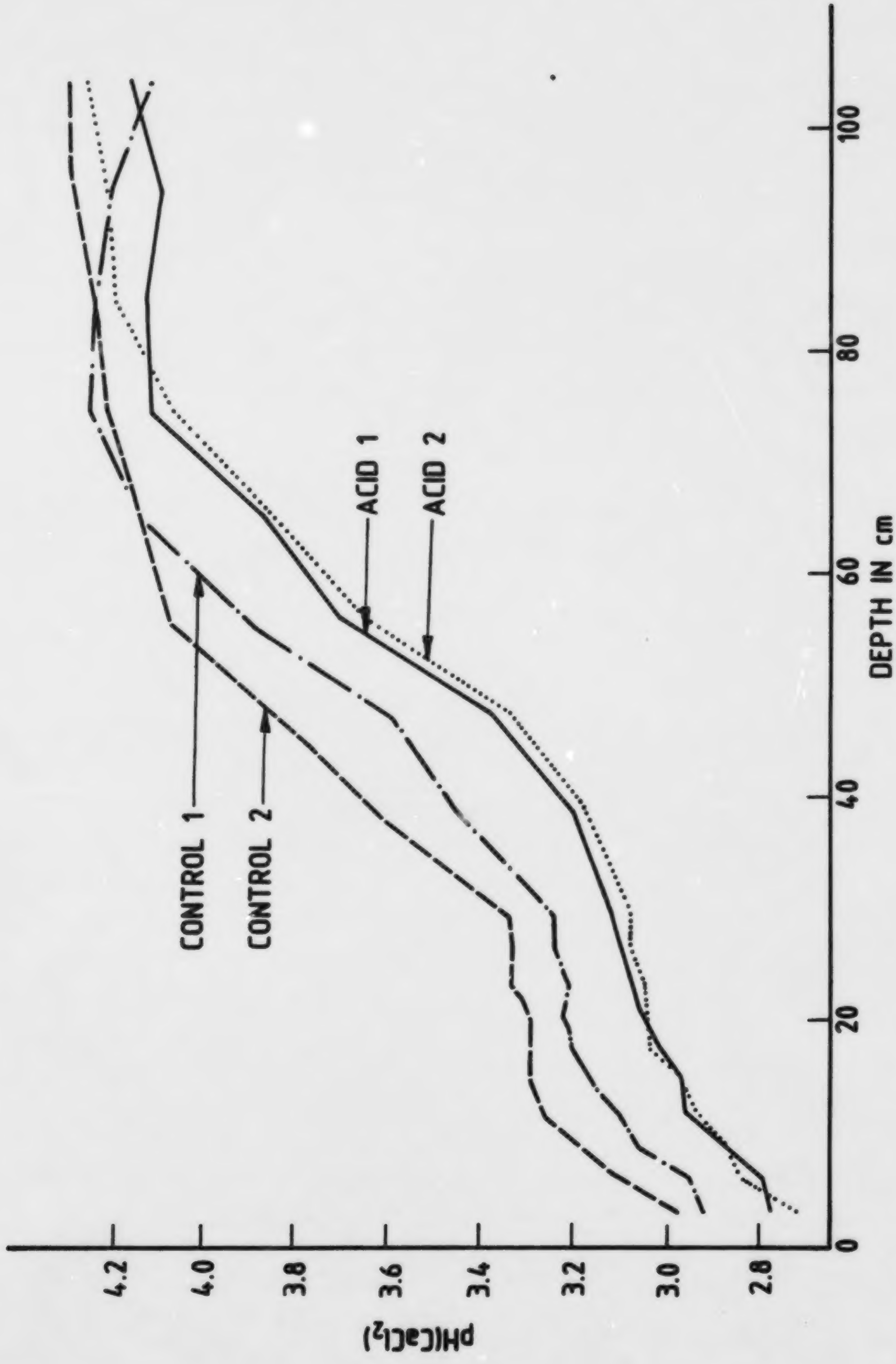

Figure 1. Depth distribution of pH (Ca C1$_2$).

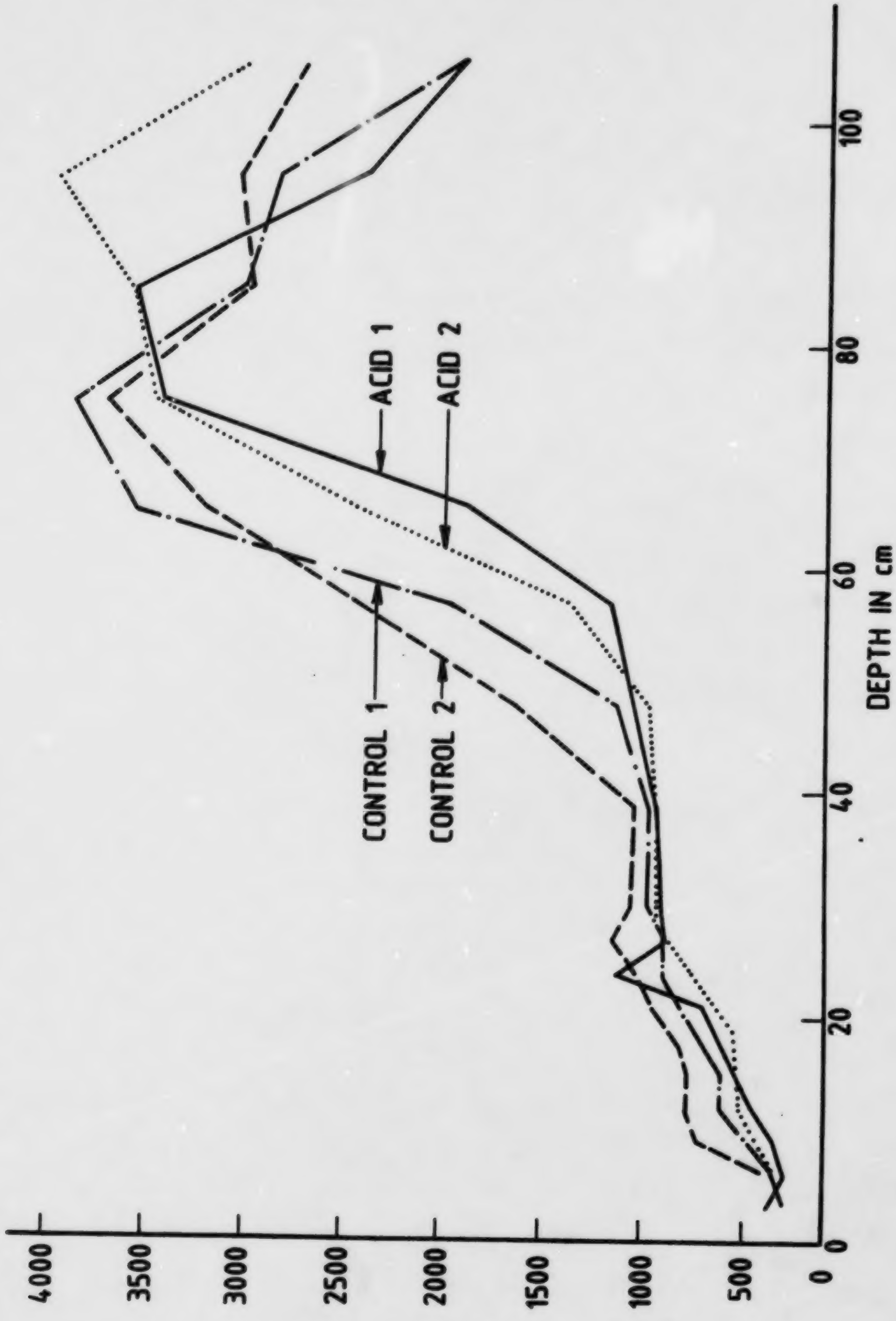

Figure 2. Depth distribution of extractable aluminum.

Table 3

Property *	Controls	Acid-treated
ATP content, $\mu g\ g^{-1}$ dry OM**	10.8	7.2
Respiration rate, μmoles CO_2 7 $days^{-1}$ g^{-1} dry OM	246	113
Glucose mineralization, n moles h^{-1} g^{-1} dry OM	7.53	6.00
Urea mineralization, n moles h^{-1} g^{-1} dry OM	41	21
Phosphatase, μmoles h^{-1} g^{-1} dry OM	39	21
Chitinase, μmoles h^{-1} g^{-1} dry OM	3.1	2.6
Xylanosidase, μmoles h^{-1} g^{-1} dry OM	1.9	1.6
Peroxidase, μmoles h^{-1} g^{-1} dry OM	7.4	0.87

* The data are the means of triplicate determinations on duplicate lysimeters. The effect of acid treatment was significant at $p < 0.001$ on all the properties, except glucose mineralization and xylanosidase, where $p < 0.01$.

** OM = organic matter.

Table 4. Lysimeter and field deposition and concentration

		Deposition, keq ha^{-1} yr^{-1}		Concentration, $\mu eq\ L^{-1}$	
		H^+	SO_4^{2-}	H^+	SO_4^{2-}
Lysimeters		15.0	15.0	1000	1000
Field:	**Rain**	0.64	0.90	59	83
	Bracken	0.47	1.00	49	105
	Oak	1.31	2.31	158	279
	Birch	1.64	2.24	206	281
	Pine	6.17	6.01	1504	1465

Table 5. Effect of trees on extractable Ca, Mg, Mn and Al

Tree	Distance from trunk	Concentration in ESS, mg L^{-1}				
		Ca	Mg	Mn	Al	pH
Oaks	30 cm	7.66	1.74	0.77	8.71	2.91***
	1 m	6.10	2.36	1.02	6.73	2.98***
	5 m	4.90	2.87	0.87	6.88	3.01***
Birches	30 cm	4.81	3.33	0.92*	5.20	2.79***
	1 m	5.41	3.04	0.82*	6.04	2.86***
	5 m	3.42	1.69	0.39*	5.58	2.98***
Pines	30 cm	8.52**	2.44	0.75*	2.60**	2.65***
	1 m	7.44**	2.05	0.88*	3.58**	2.74***
	5 m	3.94**	1.38	0.51*	5.10**	2.86***

Asterisks indicate the significance of the effect of distance from the trunk in analysis of variance.

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Table 6. Deposition of ions, 17.2.83 to 29.3.83

	Cations									Anions			Dissociated Weak Acid
	H^+	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe^{2+}	Al^{3+}	Mn^{2+}	SO_4^{2-}	NO_3	Cl^-	
Bulk precipitation	21.8	57.7	19.7	12.1	51.2	4.6	0.9	3.5	0.2	60.4	37.0	86.8	5
Birch throughfall	85.4	79.6	91.9	62.4	221.0	37.8	1.7	10.4	2.9	139.0	67.8	296.0	6
Oak throughfall	122.0	60.6	156.0	81.6	230.0	66.6	2.0	13.3	11.5	361.0	46.9	327.0	12
Pine throughfall	348.0	126.0	154.0	115.0	423.0	65.4	8.3	42.9	4.7	560.0	159.0	507.0	15

All values are in equivalents ha^{1}

Impacts of Acid Rain on Two Forested Watersheds in Haute Ardenne, Belgium

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ABSTRACT

Two forested watersheds have been studied for four years in eastern Belgium. One of the two watersheds is entirely covered by softwoods, whereas the other one is partly covered by softwoods and partly by hardwoods. The aim of the study is to evaluate the impact of vegetal cover and atmospheric pollution on nutrient turnover and aquifer and streamwater chemistry. Open-site precipitation over the country is acidic. This acidity increases significantly at the level of the throughfall rain, through the interception of acidic pollutants by the vegetal cover. This interception is more pronounced for softwoods than for hardwoods, and the acidification by organic-matter mineralization seems to depend on both the nature and thickness of the organic layers. The streamwaters flowing out from the two watersheds have percolated through the mineral soil and, in this way, their acidity is to some extent neutralized. Consequently, the two watersheds accumulate annually 60 to 70% of the inputs of acidity from pollutants and organic-matter mineralization. So, it may be asked whether the mineral soil can continue to accumulate H^+ ions without compromising the future of the forest cover of the two watersheds.

INTRODUCTION

A study of the water and nutrient cycles in forested watersheds was carried out in Belgium using an interdisciplinary approach to the hydrology and forest problems in the Haute Ardenne region.

The aim of the research program was to evaluate the impact of spruce plantations established in eastern Belgium during the past century. These plantations represent 60 to 80% of the forested area in certain hydrographic basins of the country.

The effects of the disturbance caused by the spruce plantations can be expected to appear in the nutrient mobilization and movement in soil (Nihlgard 1971; Bonneau et al. 1976; Nys 1981) and subsequently in the nutrient losses to the groundwater and the stream waters of the watersheds. Because eastern Belgium, like most of Europe, receives acid rain, the interaction of acidic deposition with forest-ecosystem processes must also be considered as an important factor influencing the nutrient losses from the watersheds (Johnson et al. 1982).

MATERIALS AND METHODS

Description of the Watersheds

The experimental watersheds are located in Haute Ardenne, one of the most forested areas of Belgium. They have a mean annual precipitation of 1300 mm, and the annual temperature averages 7°C, with monthly variations between -13°C and +25°C. Two watersheds were selected for the studies, because of their vegetation. The Robinette watershed, 81 ha in size, is entirely covered by softwoods, whereas the Waroneu watershed, 83 ha in size, is partly covered by hardwoods (40%) and partly by softwoods (60%). Dominant hardwood species are beech (*Fagus sylvatica* L.), oak (*Quercus petraea* Lieblein), and birch (*Betula pendula* Roth.). Softwood species are mainly represented by Norway spruce (*Picea abies* L. Karst.) and, to a lesser extent, by Scots pine (*Pinus sylvestria* L.). Elevations range from 310 to 400 m in the Waroneu watershed and 470 to 530 m a.s.l in the Robinette watershed. The soils consist of an acidic brown earth derived from pleistocenic loess loam, belonging to the Cambisols and the Gleysols. Their humus form varies from moder to dysmoder, and their base saturation is relatively low (5 to 15%). Both watersheds are underlain by an alternating arrangement of quartzites, quartzo-phyllades and phyllades, which present numerous wrinkles and fractures. The materials likely to be aquifers are composed of fissured and faulted quartzites, as well as the weathering mantel. The aquifer reserves vary from 0 to 10 mm in the Robinette watershed, and from 4 to 29 mm in the Waroneu watershed. The difference observed in the aquifer reserves of the two watersheds is due to their hydrogeology. Indeed, the weathering-mantel depth of the Waroneu watershed ranges from 10 to 13 m, whereas it ranges from only 4 to 6 m in the Robinette watershed. Moreover, to establish the intensive plantation of spruce in the Robinette watershed has required the setting up of numerous trenches in order to drain the hydromorphic soils. These two characteristics contribute to more important subsurface runoff of water from the Robinette than from the Waroneu watershed.

Experimental Design

Within the two watersheds, two experimental forest plots were chosen to examine the chemistry of the throughfall rain and seepage water below the humus layer. Their surface area ranged from 0.5 to 3.0 ha. Two of the plots were covered by beech, the two others by spruce. Jointly, the open-site precipitation composition was studied in clearings adjacent to the different forest plots.

Samples of rain were collected in rain gauges of 55 cm^2 surface area. Twenty rain gauges were installed in each forest plot, and five gauges were placed in adjacent clearings. In each forest plot, the rain-gauge network was complemented by four funnel-type lysimeters with an interception surface area of 285 cm^2 to collect water which had percolated through the organic layers. The results obtained in the four experimental forest plots were extrapolated by taking into account the pedological and forest characteristics of the two watersheds. At the outflow of the watersheds, streamwater was sampled once every 16 hours with automatic collectors. During periods of frost, water samples were taken manually at least once a week. The observations at the different levels of the watersheds were continued for two years, between August 1979 and March 1983. This report describes the results concerning the H^+ fluxes.

RESULTS

The distribution of monthly pH values observed in the open-site precipitation is shown in Fig. 1. More than 50% of the pH values are greater than 4.0. Nevertheless, precipitation pH values lower than 3.5 were observed during some periods. Likewise, Fig. 2 shows the distribution of monthly pH values for throughfall rain below the beech and the spruce cover. Compared with the open-site precipitation, there is an increase of acidity, which is more important in the spruce than in the beech throughfall. Indeed, for spruce, pH values greater than 4.0 are scarcely observed, whereas the frequency of pH values lower than 3.5 increases clearly. The percolation of the throughfall rain through the organic layers promotes a further acidification (Fig. 3). For beech, the frequency of pH values greater than 4.0 clearly diminishes. In the case of spruce, there is again an increase in pH values lower than 3.5, but also an increase in pH values greater than 3.7.

In the stream, at the exit of the watersheds, the distribution of pH values shifts considerably, as shown in Fig. 4. In the case of the Waroneu watershed, we find a distribution of pH values very similar to that of the open-site precipitation. At the exit of the Robinette watershed, pH values greater than 4.0 are rarely recorded, and pH can be very low during certain periods.

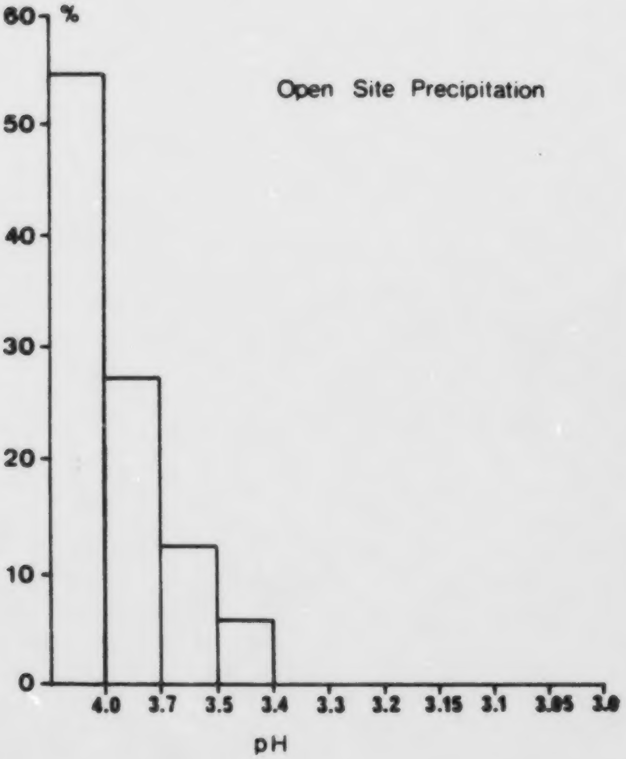

Figure 1. Distribution of monthly pH values at the level of open-site precipitation (n = 48).

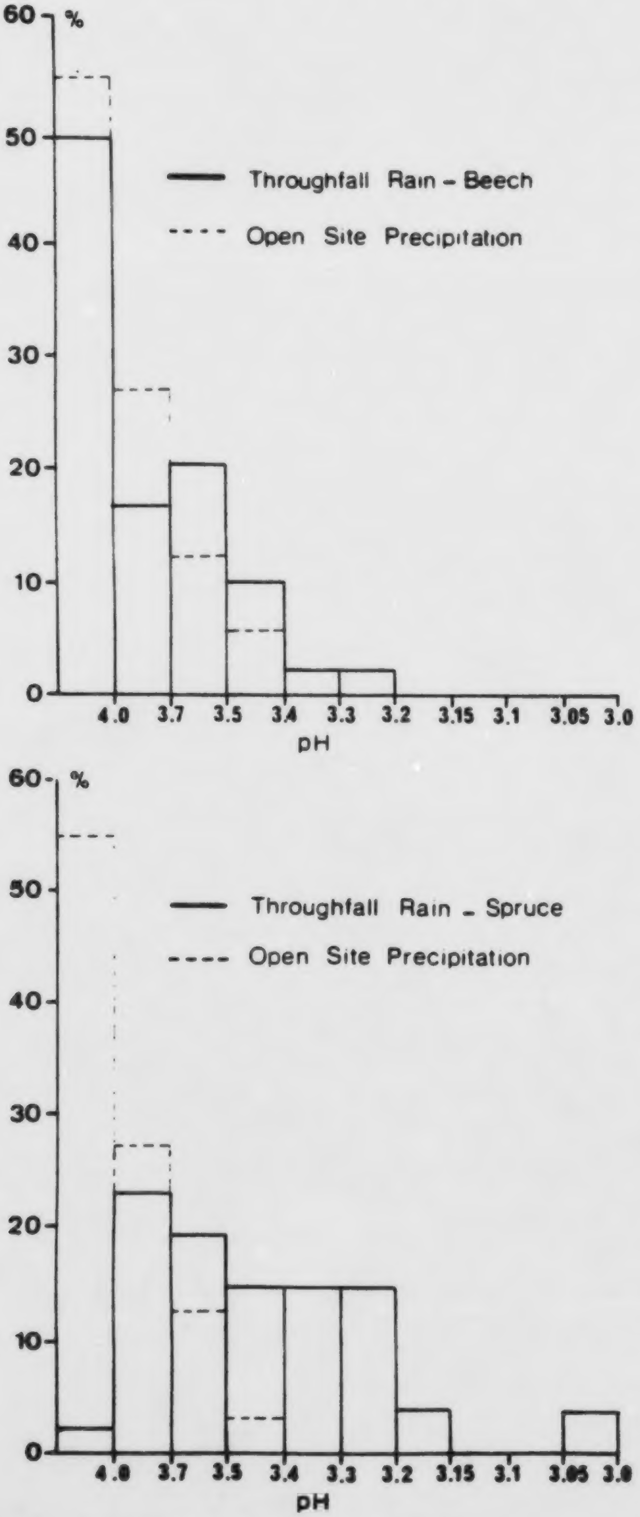

Figure 2. Distribution of monthly pH values at the level of beech and spruce throughfall (n = 48).

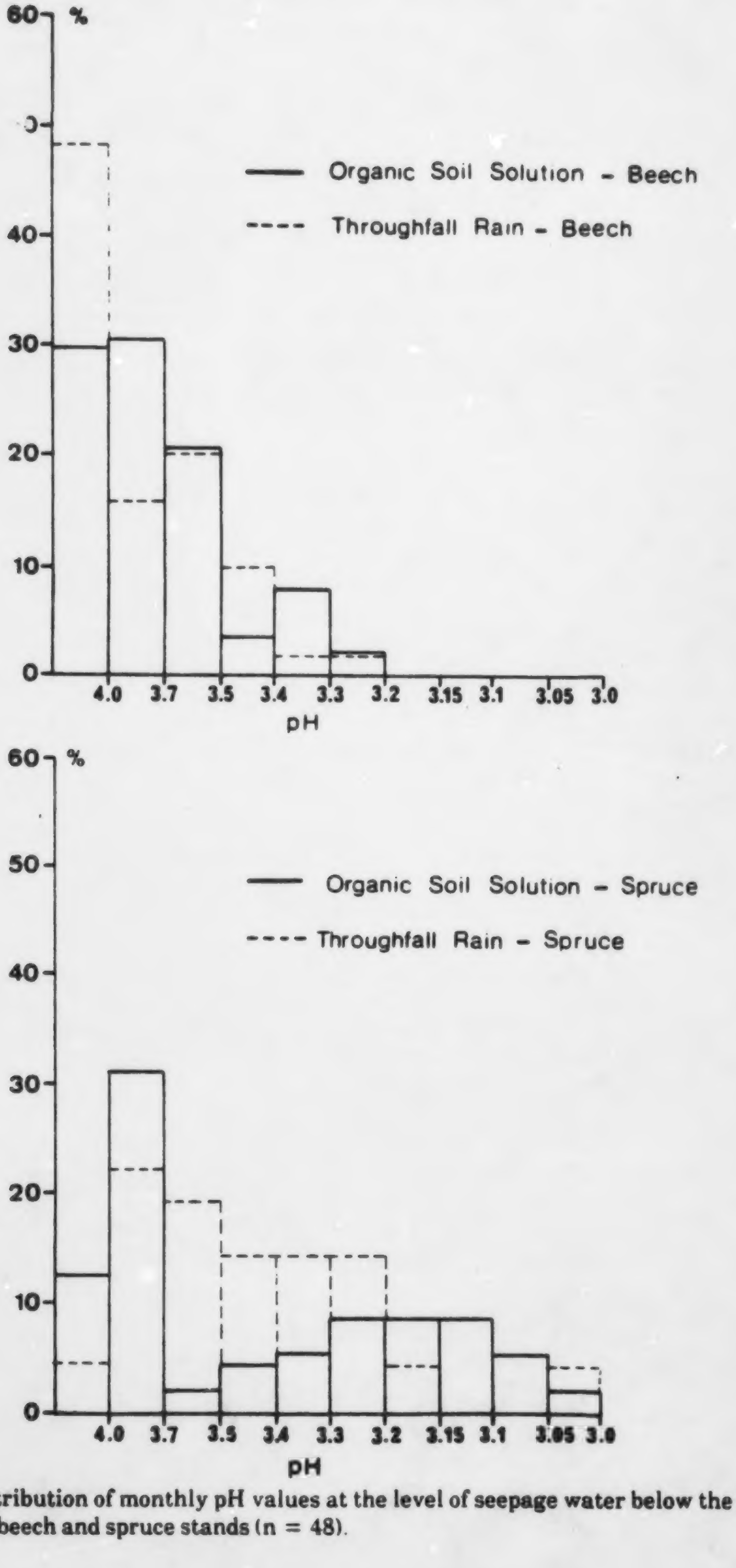

Figure 3. Distribution of monthly pH values at the level of seepage water below the humus layer of the beech and spruce stands (n = 48).

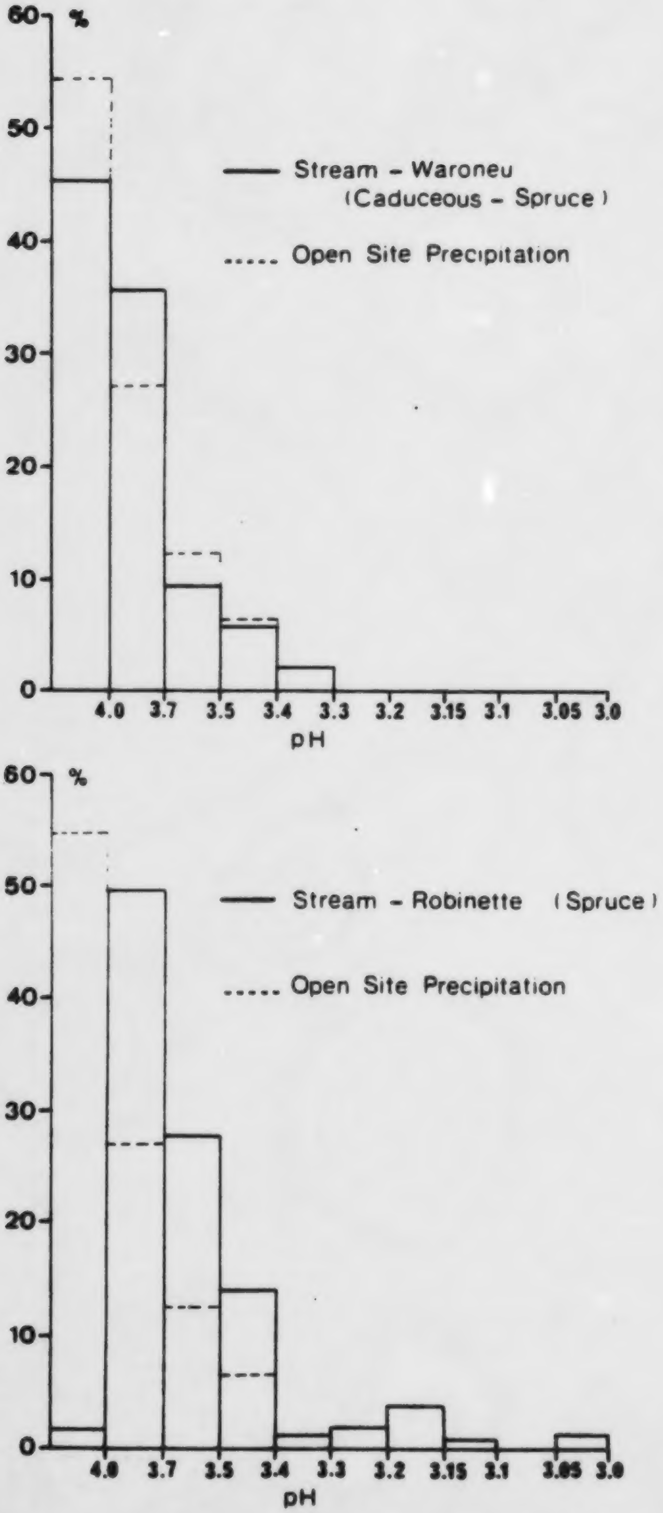

Figure 4. Distribution of pH values at the level of streams of the Waroneu and Robinette watersheds (n = 850).

Table 1. Input, output, and annual accumulation of H^+ ions for the two watersheds (kg ha^{-1} yr^{-1})

	Waroneu	Robinette
Inputs		
Precipitation	1.5	1.5
Interception of dry and gaseous deposits by the vegetation	0.8	1.6
Organic-matter mineralization	0.1	0.4
Input to the mineral soil	2.4	3.5
Output via the stream	0.7	1.4
Annual accumulation	+ 1.7	+ 2.1

Table 1 shows the H^+ input, output, and annual balance for the two watersheds. In the case of the Waroneu watershed, covered partly by deciduous and partly by coniferous species, the more important H^+ input comes from precipitation. The interception of dry and gaseous deposits increases this H^+ input by about 50%. In contrast, the H^+ inputs caused by precipitation and those caused by the interception of gaseous and dry deposits are equivalent in the case of the Robinette watershed, which is entirely covered by coniferous species. In both cases, the further acidification by organic-matter mineralization seems to be limited with respect to atmospheric H^+ inputs. The Robinette watershed releases about twice as many H^+ ions as the Waroneu watershed. The annual accumulation of H^+ ions occurs mainly within the mineral soil of both watersheds and represents 60 to 70% of the annual input.

DISCUSSION

The results of the present study clearly show that two forested watersheds in the Haute Ardenne (Belgium) receive considerable amounts of acidity by means of precipitation. Moreover, at the level of the throughfall rain, this acidity becomes more pronounced by the interception of dry and gaseous deposits by the forest canopies. This interception is significantly more important in coniferous than in deciduous forest stands, as noted in earlier studies (Nihlgard 1970; Mayer and Ulrich 1977). A further acidification by organic-matter mineralization seems to depend not only on the nature of the organic layers, but also on their thickness. Indeed, these two factors control the effectiveness of the microbial and physico-chemical processes within the organic layers (Dwyer and Merriam 1981; Buldgen et al. 1983). So, the organic-matter mineralization does not seem to promote more acidity in coniferous than in deciduous forest stands.

Since the increase in acidity by organic-matter mineralization due to the atmospheric H^+ inputs is limited, the acidity of precipitation and the ability of the forest cover to intercept dry and gaseous deposits are two important factors determining the H^+ inputs to a forested watershed.

Streamwater acidification is more significant in the Robinette watershed. This fact corresponds with the higher H^+ inputs promoted by the coniferous cover. But, as we have noted previously, the two watersheds differ in their hydrogeology. The Robinette watershed has more significant subsurface outflows than the Waroneu watershed. Therefore, the residence time of water within the Robinette watershed is shorter than in the Waroneu watershed. Consequently, it can be supposed that the buffering reactions are more effective within the Waroneu watershed, whereas the H^+ ions leave the Robinette watershed more rapidly. These views are in accordance with those of Nilsson et al. (1982). Our findings indicate that the Waroneu watershed accumulates 71% of the H^+ inputs, whereas only 60% of the H^+ inputs are buffered within the Robinette watershed. So, both watersheds capture important amounts of H^+ ions. This accumulation undoubtedly involves ion displacement and weathering reactions (Cronan and Schofield 1979; Lewis and Grant 1979). The long-term effects of this accumulation on forest ecosystems have been stressed by several studies (Abrahamsen et al. 1976; Ulrich et al. 1980).

Finally, it must be noted that acidification by cation uptake by trees has not been considered in the present study. In fact, the rate of this type of acidification depends strongly on the nature (NH_4^+ or NO_3^-) of the nitrogen nutrition (Ulrich 1981) and remains, therefore, difficult to evaluate.

ACKNOWLEDGEMENT

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Soil And Bedrock Characteristics of Eastern Canada: Acidic Deposition and Implications for Forest Productivity

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ABSTRACT

Available soil and bedrock data for eastern Canada (east of the Ontario – Manitoba border) have been combined into eight map units representing five dominant terrain types. Three of these five categories describe dominant soil texture: sand, loam, and clay. Organic soils and barren terrain ($\geq$75% bedrock outcropping) are the remaining two categories. Given the absence of proven cause and effect relationships between acidic deposition and forests, it is considered preferable to map terrain characteristics rather than forest - productivity sensitivity. Hypothetical sensitivity interpretations are provided for sensitivity to: 1) base-cation loss, 2) soil acidification, and 3) aluminum solubilization. These sensitivities are based on predicted or expected soil properties (pH and CEC) for each map unit. It is suggested that those areas mapped as sand overlying any rock type or loam overlying granite (primarily acid Podzols and Brunisols) are the most sensitive with respect to forest productivity. This interpretation assumes that Al^{3+} solubilization and the loss of even small amounts of nutrient cations are the most significant factors potentially impacting forest systems. The map base is, however, sufficiently flexible to allow other interpretations.

INTRODUCTION

The link between anthropogenic acidic deposition and its effects on forest productivity is not well defined. Although a cause–effect relationship has yet to be scientifically documented, circumstantial evidence is accumulating. Ulrich et al. (1980) have shown that in recent years, serious dieback of beech (*Fagus silvatica*) has occurred in areas of West Germany receiving high inputs of hydrogen ions (H^+). This has been attributed to sulfur dioxide (SO^2) emissions. It is believed that increased aluminum ion (Al^{3+}) concentration in the soil solution (the result of H^+ ion input to the soil body) is toxic to the fine roots of these trees, causing premature death. High Al^{3+} levels have been measured in soils at Panther Lake in the Adirondack Mountains of New York and at Mt. Moosilaukee, New Hampshire (Cronan and Schofield 1979; Cronan 1980; McFee and Cronan 1982). Johnson and Siccama (1983) have identified a significant decline in red spruce (*Picea rubus*) tree-ring widths over the last 20 years at various locations in the northeastern United States. It is highly likely, therefore, as noted by McFee and Cronan (1982), that "... if current inputs of SO_4^{2-}, NO_3^- and acid are replacing centuries of input less acid and lower in SO_4^{2-} and NO_3^-, then new trends will develop and a new balance between gains, losses and productivity will be established". The specific mechanisms by which forest changes will be effected, as well as the predicted geographic range over which these effects will be noted, have yet to be determined.

There are numerous mechanisms by which anthropogenic acid depositions might affect forest productivity. Soil acidification is a primary concern because it may have direct effects on roots as well as indirect effects by means of Al^{3+} toxicity, base-cation loss, decreased phosphate availability, changes in decomposition, and nitrogen status as related to changes in species diversity and abundance of micro-organisms, and so on (Aber et al. 1982; McFee and Cronan 1982). Changes in forest productivity may be triggered by any of these mechanisms, by climatic and environmental conditions, or by any combination of acidification mechanisms, climate, and site factors. Hence, it is extremely difficult to isolate cause and effect relationships between forest productivity and atmospheric acid deposition in natural ecosystems.

TERRESTRIAL SENSITIVITY

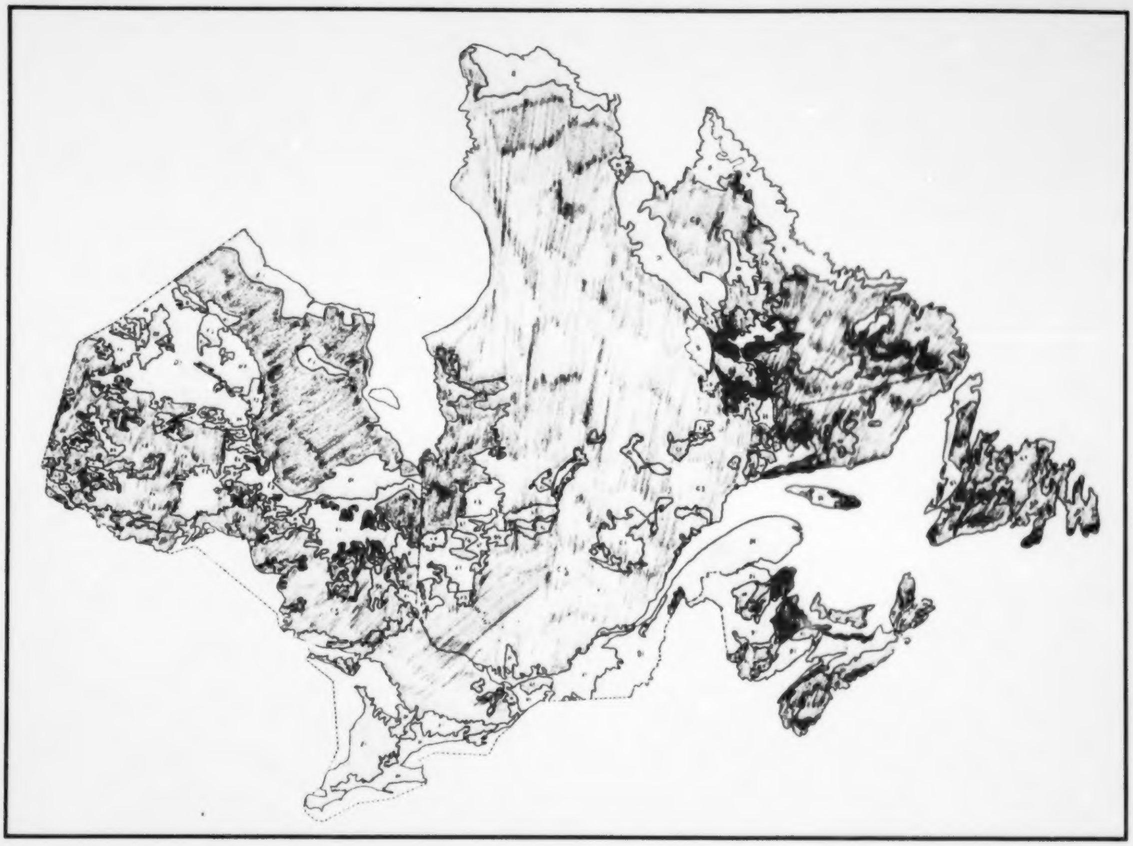
Terrestrial sensitivity has been defined in terms of forest productivity (Cowell et al. 1981) and in terms of soil acidification (Wiklander 1973/74, 1980). In both cases, effects within the soil body were emphasized. Cowell et al. (1981) regarded low-pH soils as the most sensitive ones based on the fact that these already had the smallest reserve of nutrient cations. It is assumed that additional losses of nutrient cations, however small, would be significant with respect to forest productivity in these acid soil systems. This sensitivity assessment concentrated on the upper 25 cm of the soil profile where (at least in boreal ecosystems) nutrient cycling is most efficient. Acid soils are known to actively adsorb SO_4^{2-}, thereby reducing cation mobilization. They are considered less sensitive than nonsulfate-adsorbing soils (Johnson and Cole 1977; Singh et al. 1980).

The sensitivity concept suggested by Wiklander (1973/74, 1980) predicted noncalcareous, moderately acid sandy soils (pH 5–6) with low cation exchange capacities to be the most sensitive. Wiklander derived these criteria from laboratory studies in which he found that the cation displacing efficiency of H^+ was greatly diminished as base saturation and pH decreased. Thus, for a given H^+ input, very acid soils would yield fewer cations and are classed as less sensitive than moderately acid soils. Moderately acid soils with low cation exchange capacity (i.e., less buffering by exchange sites) would experience more rapid pH change than very acid soils with the same exchange capacity. This concept of assessing soil acidification potential, in which the most sensitive soils are those experiencing the greatest change in their inherent properties, is specifically a soil sensitivity evaluation. No cause–effect relationships with vegetative or aquatic systems are specified.

If one assumes that a reduction in forest productivity is due to anthropogenic mineral acid deposition, then some consideration must be given to the possible mechanisms by which it occurs in order to assess forest ecosystem sensitivity. The term 'sensitivity' can be confusing. An overall sensitivity rating which encompasses all possible effects and mechanisms cannot be defined. Differing properties of the ecosystem or differing ecosystems will often be affected by the same pollutant in various ways depending upon the interpretation of 'sensitivity'. For example, a particular soil may be highly sensitive to base-cation leaching but nonsensitive to Al^{3+} solubilization. Thus, it is necessary to define carefully the ecosystem property being considered. For this reason, and without conclusive cause–effect definitions, it is preferable to map key ecosystem properties when mapping sensitivity. Appropriate interpretations with respect to the many possible sensitivities can be made separately and updated or modified as new evidence is obtained. This approach to sensitivity mapping has been applied to eastern Canada.

MAPPING METHODOLOGY

In Canada, especially on the Canadian Shield, soils are quite variable in thickness and often thin to discontinuous. Forest growth in such areas depends on the bedrock to provide both the substrate and the only "store" of nutrient cations. Terrestrial assessments in Canada need to include both soil and bedrock information. Figure 1 shows combinations of soil and bedrock characteristics, which may be interpreted with respect to terrestrial sensitivities. This map is a generalized version of a more detailed mapping base prepared for Working Group 1 (Impact Assessment) of the United States/Canada Memorandum of Intent (MOI 1983). The map was originally compiled at a scale of 1:1 000 000; some detail has been sacrificed at the scale reproduced here (approximately 1:10 000 000). The concept and methodology employed in the multifactor mapping is described in detail in the MOI (1983) and Lucas and Cowell (1983). Terrestrial factors included in the mapping are those suggested by Cowell et al. (1981). The factors, along with their corresponding data sources, are shown in Table 1. Because of a lack of soil chemical data for soils outside the limited agricultural areas in Canada, soil texture and depth to carbonate data have been employed (Table 1). These are the only surrogates available for soil chemistry at the scale of compilation (1:1 000 000).



	SOIL CATEGORY	TERRAIN CHARACTERISTICS	MAP AREA km²	MAP AREA % Eastern Canada
■	Organic Soils (predominantly Organic and Gleysols)	Organic soils covering ≥25% of map unit overlying bedrock types 1, 2, 3 or 4.	441,941	14.11
☐	Barren	Type 1, 2, 3 or 4 bedrock exposed in ≥75% of map unit	108,735	3.47
▨	Sand or No Lime (predominantly acid Podzols)	C1 - Soils ≥25cm thick overlying type 1, 2 or 3 bedrock.	435,686	13.91
		C2 - Soils ≥25cm thick overlying type 4 bedrock.	1,362,454	43.42
D1 / D2	Loam or Low Lime	D1 - Soils ≥25cm thick overlying type 1, 2 or 3 bedrock.	287,183	9.16
		D2 - Soils ≥25cm thick overlying type 4 bedrock.	184,557	5.89
E1 / E2	Clay or High Lime (predominantly Luvisols and Gleysols)	E1 - Soils ≥25cm thick overlying type 1, 2 or 3 bedrock.	190,842	6.08
		E2 - Soils ≥25cm thick overlying type 4 bedrock.	116,260	3.71

Bedrock sensitivity classes were defined by Shilts et al. (1981) on the basis of lithology.

Type 1 - Limestone, marble, dolomite.

Type 2 - Carbonate-rich siliceous sedimentary: shale, limestone; non-calcareous siliceous with carbonate interbeds: shale, siltstone, dolomite; quartzose sandstone with carbonates.

Type 3 - Ultramafic rocks, serpentine, non-calcareous siliceous sedimentary rocks: black shale, slate, chert; gabbro, anorthosite: gabbro, diorite, basaltic and associated sedimentary: mafic volcanic rocks.

Type 4 - Granite, gneiss, quartzose sandstone, syenitic and associated alkalic rocks.

Figure 1

Table 1. Terrestrial factors and associated criteria limits to assess forest productivity sensitivity (after Cowell et al. 1981)

Terrestrial factors	Sensitivity		
	Low	Moderate	High
Soil chemistry			
i) Exchangeable bases surrogates:	> 15 meq/100 g	6 to 15 meq/100 g	< 6 meq/100 g
(a) Family particle size and pH in water	clayey, > pH 5.0 loamy, > pH 5.5 all calcareous soils	clayey, pH 4.5 to 5.0 loamy, pH 5.0 to 5.5 sandy, >pH 5.5	clayey, <pH 4.5 loamy, < pH 5.0 sandy, < pH 5.5
(b) Texture	clay, silty clay, sandy clay (> 35% clay)	silty clay loam, clay loam, sandy clay loam, silt loam, loam (10 to 35% clay)	silt, sandy loam, loamy sand, sand (< 10% clay)
(c) Cation exchange capacity	> 25 meq/100g	10 to 25 meq/100g	< 10 meq/100g
ii) SO_4^{2-} adsorption capacity	high sulfate adsorption: low organic matter *and* high Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$ content	———	low sulfate adsorption: high organic matter *and/or* low Al_2O_3 and/or $Fe_2O_3 + Fe_3O_4$ content
Soil depth*	> 25 cm	> 25 cm	< 25 cm
* If soil depth is less than 25 cm, underlying material is incorporated			
Underlying material			
i) Parent material	carbonate bearing	noncarbonate bearing	noncarbonate bearing
ii) Bedrock material	limestone, dolomite, and metamorphic equivalents, calcareous clastic rocks, carbonate rocks interbedded with noncarbonate rocks	volcanic rocks, shales, greywackes, sandstones, ultramafic rocks, gabbro, mudstone, metaequivalents	granite, granite gneiss, orthoquartzite, syenite

Table 2. Potential sensitivities to base-cation loss, soil acidification, and aluminum solubilization by predicted soil properties as defined by map units for eastern Canada

Map unit	Bedrock type	Soil category	Predicted soil properties		Sensitivity to:		
			pH	CEC	Base-cation loss	Soil acidification	Aiuminum solubilization
A	1,2,3 or 4	Organic	< 5	High	Low–Moderate(?)	Low(?)	Low–Moderate(?)
B	1				High	Low–Moderate	Low–Moderate
	2,3				High	High	Moderate
	4				Moderate	Low	High
C_1	1,2 or 3	Sand	> 5	Low	High	Low–Moderate	Low–Moderate
C_2**	4	Sand	< 5	High	Moderate	Low	Moderate–High
			< 5	Low	Moderate	Low	High
C_2	4	Sand	< 5	High	Low	Moderate	Moderate–High
			< 5	Low	Low	High	High
D_1	1,2 or 3	Loam	> 6	Low	High	Low–Moderate	Low–Moderate
			> 6	High	High	Low	Low
D_2	4	Loam	< 5	High	Moderate	Low	Moderate–High
			< 5	Low	Moderate	Low	High
			5–6	High	High	Moderate	Moderate
			5–6	Low	High	High	Moderate
D_2**	4	Loam	< 5	High	Low	Moderate	Moderate–High
			< 5	Low	Low	High	High
E_1	1,2 or 3	Clay	> 6	High	High	Low	Low
E_2	4	Clay	> 6	High	High	Low	Low

* Bedrock sensitivity classes were defined by Shilts et al. (1981) on the basis of lithology.

Type 1 – Limestone, marble, dolomite.

Type 2 – Carbonate-rich siliceous sedimentary: shale, limestone; noncalcareous siliceous with carbonate interbeds: shale, siltstone, dolomite; quartzose sandstone with carbonates.

Type 3 – Ultramafic rocks, serpentine, noncalcareous siliceous sedimentary rocks: black shale, slate, chert; gabbro; anorthosite: gabbro, diorite; basaltic and associated sedimentary: mafic volcanic rocks.

Type 4 – Granite, gneiss, quartzose sandstone, syenitic and associated alkalic rocks.

** Sulfate-adsorbing soils.

Figure 1 was developed by recombining the 62 terrain classes mapped on the 1:1 000 000 scale base map into eight map units representing differing soils and soil/bedrock combinations, which could easily be shown at the scale reproduced here. These have in turn been grouped into five soil categories for ease of interpretation: 1) organic soils, 2) barren areas (≥75% bedrock outcropping), 3) sandy soils, 4) loamy soils, and 5) clayey soils.

DISCUSSION

Table 2 shows the eight map units illustrated on Figure 1 and their corresponding bedrock type and soil texture. Two classes of sulfate, adsorbing soils (C_2 and D_2) are also listed for completeness, although they are not mapped. For each of the map units having ≥75% exposed bedrock, soil pH and CEC combinations most likely to occur are shown. Hypothetical sensitivity interpretations with respect to base-cation loss, soil acidification, and Al^{3+} solubilization are provided for each map unit and set of predicted soil properties. These interpretations are meant only as a guide and may need to be modified as empirical data are obtained. The sensitivities are relative in terms of the magnitude of soil changes. For example, a slight change in pH of an acid soil (low sensitivity to acidification) may produce a significant increase in aluminum solubility (moderate–high sensitivity). Table 2 relates only to soil properties; forest-productivity sensitivity is not indicated.

Organic Soils

Organic soils dominate map units in 14.1% of eastern Canada. It is uncertain what effect, if any, acidic deposition has on these soils. In Table 2 they are interpreted on the basis of having high CEC and low pH. Sensitivities are shown as low-to-moderate for all three soil effects. This assumes the soils have low base-cation and metal (Al^{3+}) contents. It should be noted that many organic deposits have peat and groundwater pH values well in excess of 5. Almost one half of the organic soils overlie carbonate bedrock (6.5%). These occur primarily in the Hudson Bay Lowland where large areas of minerotrophic peatlands are found, especially in coastal areas (Sims et al. 1982). However, the peatlands of the Lowland do not have commercially viable forest stands.

Barren Areas

These are areas dominated (≥75%) by exposed bedrock. Sensitivity interpretations (Table 2) are based on bedrock lithology and do not consider differences in weathering rates. Most of these barren areas lie above the treeline and are of little consequence with respect to forest productivity. They make up about 3.5% of eastern Canada (Figure 1).

Sand or No-lime Soils

These soils (C_1 and C_2) occupy over 57% of eastern Canada and include some of the most commercially important forest areas, sand overlying granite (C_2) forming the largest single class (43%). According to the Soil Map of Canada (Clayton et al. 1977) these areas are primarily Humo-Ferric Podzols, "Rockland" (≥60% exposed bedrock), and Dystric Brunisols. These soil types (especially C_2 soils) have acidic surface horizons (pH < 5.5, dominantly < 5). They are thus considered to have a low sensitivity to acidification, a moderate sensitivity to base-cation loss, and a moderate-to-high sensitivity with respect to Al^{3+} solubilization. Some areas of C_1 soils, particularly those overlying carbonate bedrock, likely have a higher pH. These would have a high potential to lose base cations but only low-to-moderate potential to acidify or have increased aluminum mobility.

Boreal and north temperate Podzols are characterized by the accumulation of organic matter and Fe and Al sesquioxides (Stobbe 1968). Although high Fe and Al contents are properties known to enhance sulfate adsorption (Johnson and Cole 1977), high organic matter tends to block any adsorption process (Johnson and Henderson 1979). Low-pH, high-CEC podzols in eastern Canada probably do not adsorb sulfate significantly because their CEC is primarily controlled by organic matter. At this time, however, there is very little experimental evidence regarding the sulfate-adsorption capacity of Canadian soils.

Loam or Low-lime Soils

D_1 and D_2 soils occupy about 15% of eastern Canada located primarily in northwestern and southern Ontario, southern Quebec, and New Brunswick. They are mapped by Clayton et al. (1977) primarily as Podzolic and Brunisolic. These soils are considered to exhibit a wide range of soil properties from very acidic (in boreal areas) to basic (those overlying carbonates).

Clay or High-lime Soils

These soils cover 9.7% of eastern Canada primarily in Ontario. They are interpreted as having a low sensitivity with respect to soil acidification and Al^{3+} solubilization. However, sensitivity to base-cation loss is high. According to the Soil Map of Canada (Clayton et al. 1977) these soils are primarily Gray Luvisols and Gleysols (clay-rich and/or under periodic or seasonal flooding).

IMPLICATIONS FOR FOREST PRODUCTIVITY

Figure 1 shows combinations of soil texture and bedrock type in eastern Canada. Soil texture is included as a surrogate for soil chemistry as suggested by Cowell et al. (1981) and Lucas and Cowell (1983). According to this scheme, sandy soils represented low-pH, low-CEC soils and were assigned a high sensitivity rating for forest productivity (Table 1). It is acknowledged, however, that many loam soils, particularly loamy tills in boreal and mixed forest regions, have low pH (< 5.0) in the upper 25 cm of the profile (class D_2, Table 2).

The most sensitive areas in eastern Canada with respect to forest productivity suggested to be those areas mapped as C_1, C_2 are, and D_2 (Figure 1). These soils are considered to have the greatest potential for Al^{3+} mobilization given that the most acid Podzols and Brunisols in eastern Canada have the highest amounts of Fe and Al sesquioxides. As noted above, SO_4^{2-} adsorption is not considered significant in young glacial soils (Abrahamsen 1980). Table 2 indicates that these soils have low-to-moderate sensitivities to base-cation loss. This is relative to expected higher losses in soils richer in base cations. Because the low-pH soils are already impoverished in these nutrients, it is assumed that any additional loss would have serious consequences to forest productivity.

Although areas mapped as C_1, C_2, and D_2 are considered the most sensitive with respect to forest productivity, they are not equally susceptible throughout the map area. Effects depend on the concentration and total amount of acids received, hence the most susceptible forest areas are those mapped as C_1, C_2 or D_2 in areas receiving the highest acid loading. Generally the loadings increase toward the south and southeast; southern and central Ontario, southern Quebec, and the Maritimes receive the highest impact. Figure 1 can be compared to the pollutant loading maps provided in the MOI Working Group 1 Report (MOI 1983) in order to relate soil bedrock conditions to deposition patterns in eastern Canada. It is not known at this time what loading dose will produce effects.

CONCLUSION

There is no doubt that acidic deposition is a stress to forest ecosystems through both direct and indirect processes. The only question relates to the seriousness of this stress on productivity in the long term, especially when superimposed on stresses provided by climate, forest harvesting, insect and fungal diseases, and other pollutants. The base map from which Figure 1 was derived (MOI 1983) is sufficiently flexible to allow other interpretations for forest, productivity sensitivity than that provided here.

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An Experiment to Assess the Sensitivity of Soil to Acidification

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ABSTRACT

In an experiment, surface soil horizons from a variety of soil types across Ontario were treated with acidic reagents (nitric, sulphuric, nitric-sulphuric and simulated rain). Soil pH was then measured to determine the relative sensitivity of soil to acidification. The surface samples collected from Podzolic soil profiles had pHs below 4.5. They were the least sensitive to acidification, possibly due to their abundance of organic matter. Surface soils with pHs above 4.5, when combined with acidic reagents, showed greater decreases in soil pH than Podzolic soils under the some conditions. This indicates a lower buffering capacity in the less acidic soils. Within-sample decreases in soil pH were largely a function of the type of acid added to the soil. Generally, nitric acid was the most effective in lowering soil pH in these surface soils while sulphuric acid was the least effective. Further experimentation using subsurface horizons is required to fully assess the sensitivity of soil to inputs of atmospheric acidity.

INTRODUCTION

The examination of a soil's sensitivity to acidification is crucial to the study of the effects of acidic precipitation on terrestrial and aquatic ecosystems. The soil acts as a reservoir or a source of elements to aquatic ecosystems. It is also a substrate on which vegetative growth depends. Soil types react differently to acidification due to their chemical and physical properties. Wiklander (1973/74) suggested that Brunisolic soils (slightly to medium acidic) may be more sensitive to atmospheric acidification than those soils which are extremely acidic, such as Podzolic soils. Other researchers, — Wang and Coote (1981), McFee (1980), Cowell et al. (1981) — have proposed that Podzolic soils may be the most sensitive to atmospheric acidification due to their inherently low base saturation.

The ability of a soil to resist changes in hydrogen ion concentration is known as a soil's buffering capacity. Texture, organic matter, exchangeable cations, base saturation, C.E.C., the presence or absence of carbonates, aluminum and iron hydroxides, anion adsorption capacity and mineralogy play an intricate role in determining the total buffering capacity of a soil. Tomlinson (1983) and Voigt (1980) provide a more thorough account of the main sources of buffering in soils of various pH values.

A buffering curve is generated by plotting soil pH values against the concentration of acidity or alkalinity of the reagent added to the soil. A soil's buffering ability is illustrated by the slope of the curve. In the past, buffering curves have mainly been used by agronomists to determine the lime requirement of a particular soil by measuring the increase in soil pH after additions of calcium hydroxide.

A buffering curve experiment was designed to assess the relative sensitivity of Ontario soils to atmospheric acidification. Soil pH was measured in a variety of reagents of increasing acidity. The relationships of the slopes of these curves to the physical and chemical properties of the test soils will provide a means for rating a surface soil's sensitivity to acidification.

MATERIALS AND METHODS

Surface horizons from a variety of soil types from southern Ontario were used. In summer 1982, soil pits were dug in relatively undisturbed locations on a variety of landforms and described according to the Canadian System of Soil classification (1978). Forty-four surface samples (Ah or LFH horizons) were collected for these buffering curve experiments. Soil samples were air-dried, lightly disaggregated with a mortar and pestle, and passed through a 2-mm (10 mesh ASTM) sieve. All pH measurements were made on the less than 2 mm size fraction.

Ten-gram aliquots of each soil sample were placed into 100-ml beakers. To one of the beakers and soil, 40 ml of distilled water (pH 5.6) were added. To each of the remaining beakers, 40 ml of dilute nitric acid, sulphuric acid, nitric-sulphuric acid and simulated acidic precipitation reagent, respectively, were added at either pH 4.0, 3.5, 3.0 or 2.5. Soil suspensions were then stirred three times over 30 minutes and left to equilibrate for an hour. Measurements of pH were made using an Orian pH meter (Model 601A) and a Fisher combination electrode (No. 13-639-90). The reference bridge was placed in the supernatant liquid, not in direct contact with the soil particles. After the pH value stabilized, it was recorded.

The pH values of the soil in distilled water and in the acidic reagents (pH 4.0, 3.5, 3.0 and 2.5) were plotted against the milliequivalent concentration of H^+ ion added in the reagents. Each of the four soil buffering curves was plotted on one graph for comparative purposes, using the pH of soil in distilled water as the beginning point of the dilute acid buffering curves.

RESULTS AND DISCUSSION

A decrease in soil pH was associated with increasing reagent acidity in all samples. In most cases, the pH of the soil did not show a significant decrease until the pH 3.0 and/or pH 2.5 reagents were used. Most soils were able to buffer low to moderate amounts of acidity. The total decrease in measured soil pH for all buffering curves, after the addition of 0.16 meq of H^+, ranged from as little as 0.4 of a pH unit to 2.4 pH units.

Slopes of each buffering curve were calculated after the addition of 0.16 meq H^+ to the soil. Average slope values for each reagent with acidic (pH in distilled water less than 4.5) and less acidic (pH in distilles water greater than pH 4.5) soils were derived. These results are summarized in Table 1.

Within-sample variations were a function of the solution used. In 82% of the samples, dilute nitric acid (pH 3.0, pH 2.5) caused the greatest depression of soil pH followed by the sulphuric-nitric acid mixture. In 75% of the samples, the dilute sulphuric acid reagent (pH 3.0, pH 2.5) had the least effect in decreasing soil pH values. The slopes of the four buffering curves increased, in most cases, in the order: dilute sulphuric acid, simulated acidic precipitation, dilute nitric-sulphuric acid, and dilute nitric acid (Table 1). Surface soils were better able to buffer against inputs of sulphuric acid than other acid species, such as nitric acid. Slope characteristics varied greatly between samples as a result of differences in soil buffering capacities. Data in Table 1 also indicate that acidic surface soils are better buffered against changes in soil pH than less acidic surface soils because buffering curve slopes in all reagents for acidic soils are lower than those for the less acidic test soils.

Table 1. Buffering curve slopes (calculated between 0 and 0.16 meq of H+ added to the reagent)

Reagent	Extremely acidic soils (pH < 4.5) n = 7	Less acidic soils (pH > 4.5) n = 37
Sulphuric acid	mean = 2.39 standard deviation = 0.24 range = 2.31 - 2.69	mean = 5.03 standard deviation = 1.51 range = 0.94 - 7.88
Simulated acidic precipitation	mean = 2.78 standard deviation = 0.82 range = 1.69 - 3.50	mean = 5.94 standard deviation = 2.19 range = 1.38 - 11.19
Nitric/sulphuric acid	mean = 3.39 standard deviation = 0.43 range = 2.88 - 3.81	mean = 7.50 standard deviation = 2.36 range = 1.88 - 12.19
Nitric acid	mean = 3.82 standard deviation = 0.71 range = 2.94 - 4.75	mean = 8.42 standard deviation = 2.84 range = 2.31 - 14.63

The presence of carbonates is a buffering source and an important factor in determining the initial pH of the soil. Most calcareous and clay surface soils in the experiment exhibited pH values (distilled water) greater than 6.0. The reduction in soil pH in the acidic reagents yields only slightly acidic soil pH values which would not be detrimental to the availability of nutrients to plants or induce heavy metal mobility in soils. However, the rate of change in soil pH in these soils was quite large. Texture and organic matter tend to contribute to the buffering capacity of noncalcareous surface soils of lower pH values (pH <6.0) because cation exchange capacity, base saturation and pH are governed to a large degree by these two soil properties.

Soil buffering curves of four Ah horizons from selected Podzolic and Brunisolic profiles are illustrated in Figures 1 and 2, respectively. Analytical data for these soils are provided in Tables 2 and 3.

The Podzolic-type organic horizons (pH in distilled water less than 4.5) yielded buffering curves which were only gently sloping (Figure 1). These curves illustrate the least overall change in soil pH. The Plastic Lake and Wendigo Series soils are naturally acidic. However, a small change in soil pH can induce a considerable change in soil chemistry under these acidic conditions because of solubilization of metals and the loss of base cations. The analytical data provided for the Podzolic surface samples (Table 2) suggest that these extremely acidic soil samples derive their buffering capacity from the great number of exchangeable base cations in the organic matter and the presence of organic acids. The soil's ability to resist changes in pH is probably a result of the great potential for base ion exchange in these acid, organic soils.

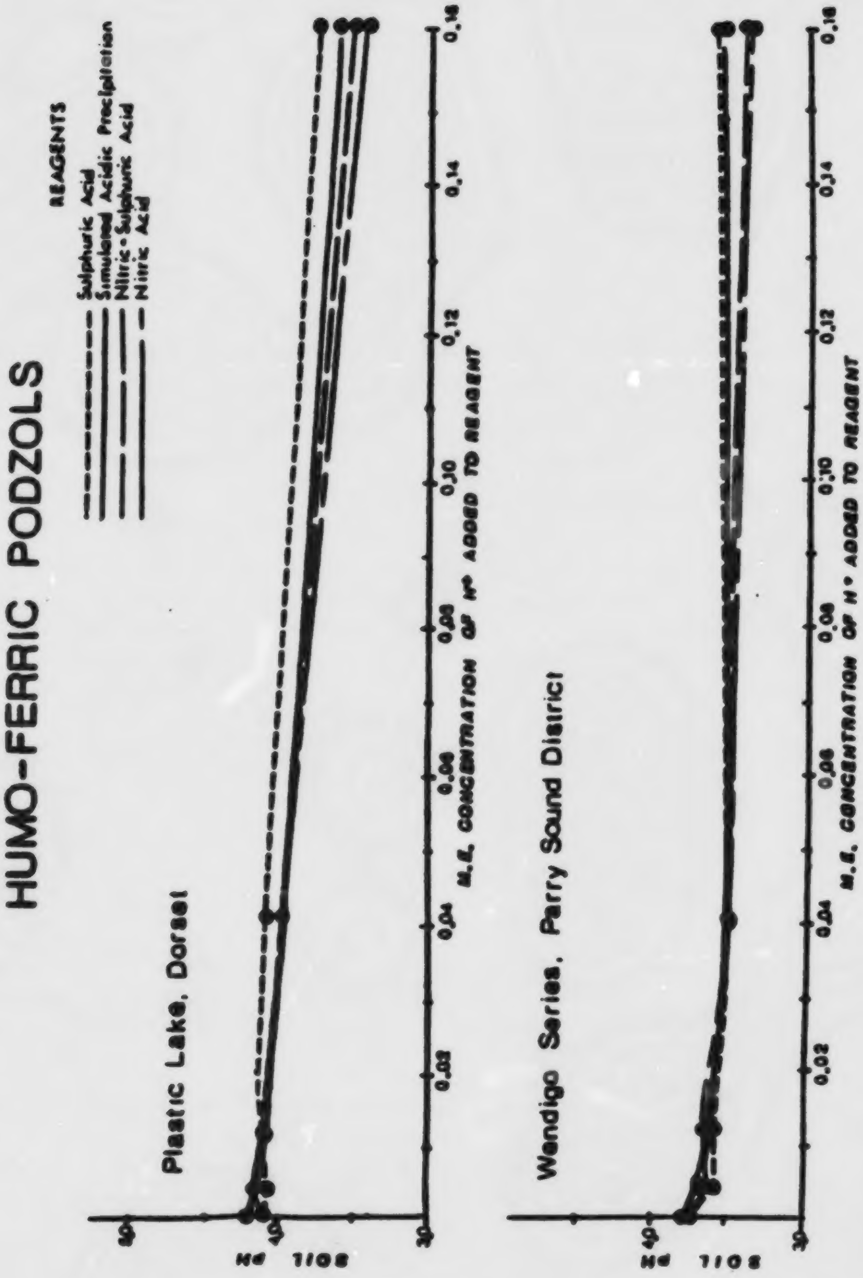

Figure 1. Soil buffering curves of Ah horizons

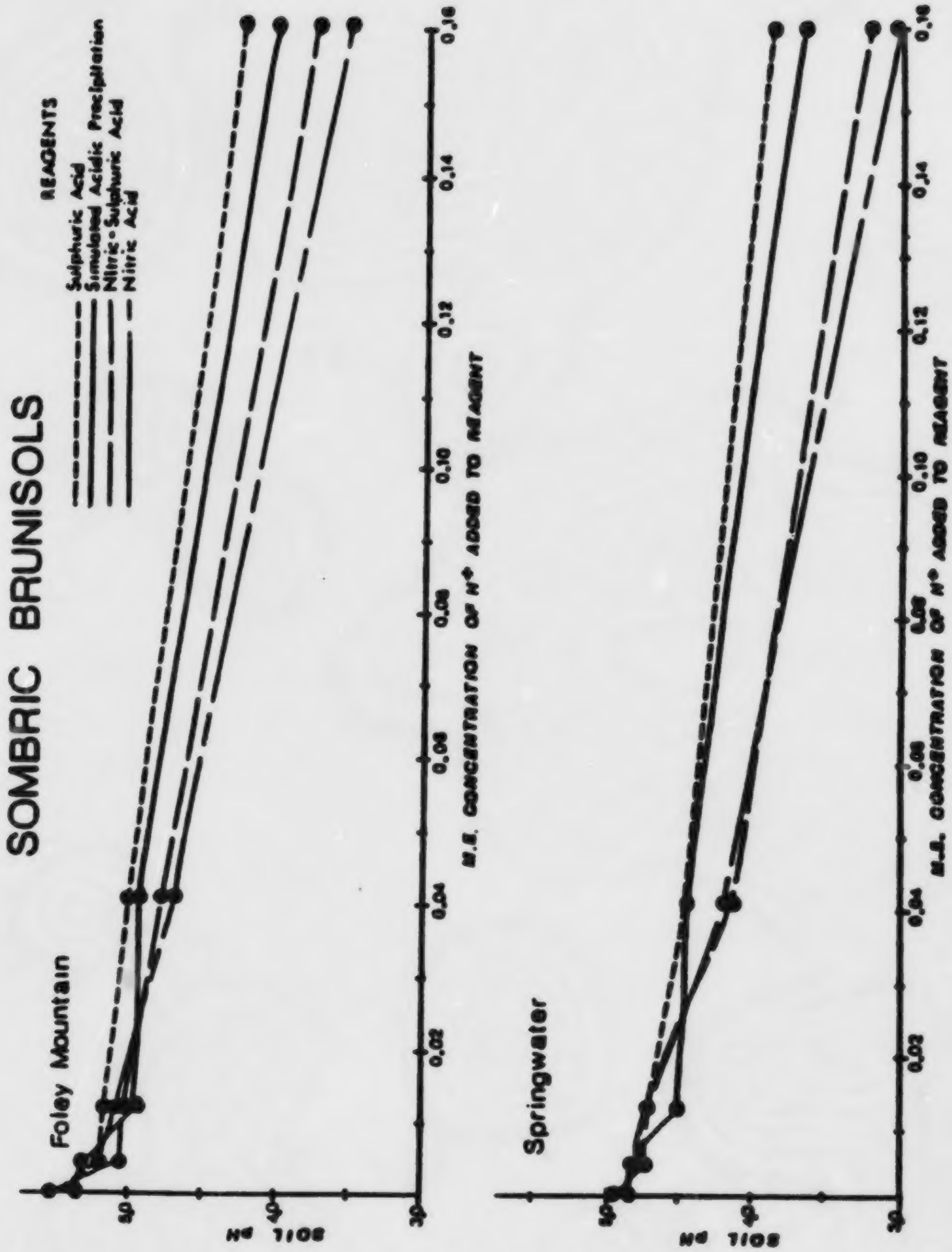

Figure 2. Soil buffering curves of Ah horizons

Table 2. Soil analytical data, humo-ferric podzols

Horizon	Depth (cm)	pH(H_2O)	pH($CaCl_2$)	Ca	Exchangeable Mg	K	Al	C.E.C. meq/100 g	Organic C %	Sand %	Silt %	Clay %
					µg/g							
Wendigo Series, Parry Sound District												
Ah	0-10	4.02	3.42	2360	340	150	140	16.32	8	15	30	55
Ah	0-10	3.92	3.47	3410	290	290	200	22.08	13	17	48	36
(duplicate)												
Plastic Lake, Dorset												
Ah	0-10	4.0	3.2	1150	150	360	310	10.91	13	44	30	27
Ah	0-10	4.2	3.5	1440	400	620	130	13.28	19	-	-	-
(duplicate)												

Table 3. Soil analytical data, Sombric Brunisols

Horizon	Depth (cm)	pH(H_2O)	pH($CaCl_2$)	Ca	Exchangeable				Organic C %	Sand %	Silt %	Clay %
					Mg	K	Al	C.E.C.				
					μg/g			meq/100 g				
Foley Mountain												
Ah	0-15	5.0	4.2	250	37	35	66	2.31	4	75	15	10
Ah (duplicate)	0-15	5.0	5.1	190	32	39	53	1.85	4	79	14	8
Springwater												
Ah	0-20	6.13	5.03	367	29	25	9	3.18	2.01	96	3	1
Ah (duplicate)	0-20	5.71	4.90	431	45	25	14	3.23	2.13	93	2	5

After an addition of 0.16 meq of H^+ to very strongly to medium acid soils (pH in distilled water is 4.6 - 6.0) the final soil pH values could cause heavy metal mobilization in soil and alter the availability of major plant nutrients (Figure 2). It is in these less acidic Foley Mountain and Springwater soils that the greatest overall change in soil properties may occur, which could in turn affect soil productivity and plant growth. The analytical data provided in Table 3 indicate that these samples contain a lower amount of organic carbon and a correspondingly lower cation exchange capacity than the Podzolic surface soils. Fewer base cations are available to exchange with inputs of acidity and the soil becomes acidified.

CONCLUDING REMARKS

In relation to atmospheric acidic deposition, Wang and Coote (1981) calculated that eastern Canada surface soils (0-15 cm) would receive, at most, 1.5 meq of atmospheric H^+ per 100 g of soil over a 25-year period. Acid concentrations from 0 to 1.6 meq H^+ per 100 g of soil were used in this experiment. The most acidic reagents in this experiment closely approximate those levels of atmospheric acidity that may be expected over a 25-year period in eastern Canada.

When the equivalent of 25 years of acidic precipitation was added to surface soil horizons, the soils with pH values greater than 4.5 demonstrated the least ability to buffer. Theoretically, then, pH reduction in surface soil samples from Brunisolic soils may affect soil productivity. The pH of extremely acidic surface soils from Podzolic soils decreased only slightly under the same experimental conditions. The buffering capacity of these surface horizons is probably derived from the nature and abundance of organic matter present. Decreases in soil pH are largely a function of the type of acid added to the soil. Nitric acid had the greatest effect in decreasing soil pH and sulphuric acid the least.

Even though the levels of acidity in this experiment can be related to those in natural acidic deposition, direct extrapolation of these experimental results to a soil's ability to buffer against atmospheric inputs in the field is theoretical. A major factor that influences the measured soil pH value is the contact time of the reagent solution and soil. Due to ion exchange phenomena, soil pH values may vary greatly over time and exact equilibration times for each soil are not known. By standardizing the time of pH measurement, inter-comparisons may be made between soil samples, but equilibration times will not necessarily be representative of field conditions. In the field, well-drained soil profiles would not become as saturated as the experimental soil. Soil suspensions were periodically stirred, increasing soil surface and reagent contact, enhancing exchange processes and altering soil pH.

Physical characteristics of the soil such as permeability and infiltration rates will determine the quantity and rate of atmospheric acidic deposition delivered in the field. These soil characteristics are controlled by vegetative cover and such soil properties as texture, structure and the nature of soil organic matter. Water movement through soil and percolate contact with soil particles are not homogeneous in the field, resulting in channeling along soil voids and fissures. In contrast, the experimental soil samples were disaggregated and sieved prior to experimentation, resulting in a more homogeneous soil than that which exists naturally.

Sensitivity of a complete soil profile and/or soil type is not feasible using only surface horizons. Further experimentation using subsurface horizons is required to fully assess the sensitivity of soils to atmospheric acidification.

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Relative Frequency of the Durations and Volumes of Ambient Rainfalls in the Eastern United States

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ABSTRACT

Acidic precipitation, wet or frozen deposition with a hydrogen ion concentration greater than 2.5 μeq L^{-1}, contributes significantly to air pollution in the United States and Canada. Effects of acidic precipitation on plant foliage may be related more to H^+ concentration than to total H^+ deposition. Because foliar injury can result from ambient rainfall and the duration of simulated rainfall is known to contribute to the extent of foliar injury, data were evaluated to characterize ambient rainfall at several locations in the eastern United States. A significant percentage (between 17 and 40%) of all showers recorded on Long Island, NY, Urbana, IL, Franklin, NC, and Seaside Park, NJ, had durations less than 40 minutes (50, 46, and 32% for three years at Urbana, IL, 65% at Coral Gables, FL, 50% at Franklin, NC, and 54% at Seaside Park, NJ). When all data from the six growing seasons were pooled, over 88% of all rainfall lasted less than 160 minutes. Similar results were observed when volume measurements were made. Between 38 and 57% of all recorded showers were less than 1 mm at all five stations in the eastern United States. When all data were pooled, over 65% of all showers were less than 3 mm. These data demonstrate that plant foliage is wetted during the growing season by numerous showers which are of short duration and low volume.

Ion Transfer Through a Tolerant Hardwood Canopy, Turkey Lakes Watershed, Ontario

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ABSTRACT

Hydrogen (H), potassium (K), calcium (Ca), nitrate-N (NO_3-N) and sulphate-S (SO_4-S) were measured, during 1981, outside and within an old-growth sugar maple (*Acer saccharum* Marsh.) - yellow birch (*Betula alleghaniensis* Britton) forest growing on an acid till soil at Turkey Lakes Watershed, Ontario. Mean concentrations and contents of elements in precipitation, throughfall and stemflow were compared on an annual, growing season and dormant season basis. Throughfall solutions were similar to precipitation in ionic composition, with the exception of K concentration, during the dormant period, and were less acid and richer in bases and SO_4-S during the growing season. Stemflow solutions were highly enriched in Ca, K and SO_4-S and depleted in H and NO_3-N, during both periods. Throughfall was the major process of element transfer to soil; stemflow accounted for only 1 to 10% of the total annual deposition of each element in the soil. The role of H in promoting base leaching from the forest canopy is discussed in relation to other eastern North American tolerant hardwood forests, which are more heavily impacted with acid precipitation.

INTRODUCTION

Interaction of precipitation with forest canopies washes nutrients from within foliage and bark and from their surfaces, thereby generally enriching water reaching the forest floor (Tamm 1951, Madgwick and Ovington 1959, Carlisle et al. 1966). Fluxes of elements in throughfall (precipitation falling through the canopy) and stemflow (precipitation flowing down the stem) are important in nutrient cycling in forest ecosystems. The quality of throughfall and stemflow water varies with forest type and with proximity to maritime, agricultural and anthropogenic activities.

In deciduous forest the quality of throughfall has a seasonal variation (Carlisle et al. 1966), related to the presence or absence of foliage and the degree of maturity of the leaves. For example, Hoffman et al. (1980) reported that throughfall pH under chestnut oak (*Quercus prunus* L.) forest in Tennessee was higher than precipitation pH during leaf-out, and equal to or less than incident pH during the leafless period. For a review of factors contributing to quality and quantity of throughfall see Parker (1983).

Both atmospheric acids and those produced naturally within terrestrial ecosystems contribute to acidification of surface waters associated with forested landscapes. Increases in acidity are commonly observed as rainwater percolates through tree crowns and forest floors, particularly in coniferous forests on acid soils (Foster 1974, Ugolini et al. 1977). Atmospheric acidity can, however, be neutralized by reactions with forest canopies (Nihlgård 1970, Eaton et al. 1973).

Further, it has been suggested that acid precipitation may accelerate the leaching of nutrients from foliage (Tamm and Cowling 1977, Tukey 1980). Increased cation leaching from leaves has been induced artificially by acidified rainwater (Wood and Bormann 1975, Abrahamsen et al. 1976). Sulphate ions in acid precipitation may ultimately increase cation mobility in soil and the likelihood of cation leaching from soil to ground and surface waters.

The influence of acid precipitation on the cycling of elements within typical forest ecosystems of eastern Canada is being examined in three Canadian Forestry Service watershed studies at Kejimkujik National Park, Nova Scotia, Montmorency Forest, Quebec, and Turkey Lakes Watershed, Ontario. This paper reports results of canopy-precipitation interaction studies in a tolerant hardwood forest at Turkey Lakes Watershed. The objective of the study is to examine the interaction of acid and acid-forming substances (hydrogen (H), nitrate (NO_3), and sulphate (SO_4) ions) in precipitation with a sugar maple (*Acer saccharum* Marsh.) canopy, with particular attention to the leaching of calcium (Ca) and potassium (K) from the foliage. Complementary studies on element distribution and fluxes in the biomass (Morrison 1984) and element outputs in streamflow (Nicolson 1984) in tolerant hardwood forests at Turkey Lakes are also presented in these proceedings.

SITE

A 1-ha study site was established within an uneven-aged sugar maple forest that has a lesser component of yellow birch (*Betula alleghaniensis* Britton), within Sub-basin 31 of the Turkey Lakes Forest Watershed (lat. 47°03'N, long. 84°25'W), Algoma District, Ontario. This tolerant hardwood stand, located within the Algoma Section (L.10) of the Great Lakes- St. Lawrence Forest Region (Rowe 1972), had an average diameter (DBH) of 19.6 cm, basal area of 28.6 m^2 ha^{-1}, stocking of 673 trees per hectare, mean dominant height of 22.1 m and mean age of 135 years.

The climate is modified continental with prevailing winds from the west. The average January temperature is -10.2°C and the average July temperature is 17.8°C (at Sault Ste. Marie, 60 km south of the watershed) (Anon 1982b). The 973 mm of mean annual precipitation (Sault Ste. Marie) are evenly distributed through the year; the wettest month is September (108 mm) and the driest is February (55 mm) (Anon 1982a).

Watershed 31 is a moderately steep, 7-ha sub-basin, at an elevation of 350 to 400 m. The soil consists of a stony, acid (pH H_2O 4.3 to 4.8), silty loam ablation till over a compacted sandy basal till at a depth of 0.5 m. Soils are Orthic Humo-Ferric and Ferro-Humic Podzols (Canada Soil Survey Committee 1978) derived from greenstone and granite.

METHODS

Three bulk precipitation collectors were located in an open area adjacent to Watershed 31. The study site in the forest contained 36 throughfall collectors and 18 sugar maple trees with stemflow collars. Precipitation and throughfall were collected in continuously open (bulk) collectors 20 cm in diameter, either plastic funnel-bottle sets or aluminum rain gauges. Stemflow was collected by a 2.5-cm plastic tree collar located approximately 1.5 m above ground level. The 18 stemflow trees were selected to cover the diameter range of 8 to 60 cm.

During the snowfree period, precipitation, throughfall and stemflow samples were collected for discrete storm 'events' or occasionally for composite events. A minimum event size of 2 mm was selected, as canopy interception in hardwood forest ranges from 0.5 to 2 mm (Zinke 1966). Snowfall was sampled every second week from three 'snowboards' outside and 12 within the forest. Throughfall samples were bulked in groups of three; i.e., 12 samples per event were taken for chemical analysis. Separate analyses were made on precipitation, stemflow and snow samples.

Concentrations and contents of H, Ca, K, nitrate-N (NO_3-N) and sulphate-S (SO_4-S) in each process were calculated for 45 sampling days during 1981. Concentrations are expressed on a volume-weighted basis in μeq L^{-1}. The results were analyzed by dividing the year into dormant season (leaves off) and growing season (leaves on). Twenty-five sample collections were made during the growing season (mid-May to mid-October) and 20 during the dormant period. The quantity of stemflow on an area basis was determined by using individual tree stemflow estimates in each diameter class (derived from sugar maple) times the number of trees (all species) in each diameter class, as estimated from four 0.1-ha permanent sample plots located within the study site.

Sulphate-S and NO_3-N were measured with a Technicon Autoanalyzer II system by the methylthymol blue and cadmium-reduction methods, respectively. Sulphate-S in highly-colored (mainly stemflow) samples was measured by ion chromatography. Cations were analyzed with an atomic absorption spectrophotometer (flame emission for K and atomic absorption for Ca). Hydrogen was calculated from glass electrode pH measurements.

RESULTS

Dormant Season

Throughfall solutions were similar in ionic composition to incident precipitation, except for enrichment in K (Table 1). Stemflow solutions, on the other hand, were highly enriched in Ca, K and SO_4, but were depleted in H and NO_3. Quantities of H, Ca, SO_4-S and NO_3-N in precipitation were relatively unchanged by passage through the forest canopy (Table 2).

Table 1. The 1981 seasonal concentrations of elements in precipitation above and below an old-growth sugar maple-yellow birch forest canopy

	Mean element concentration, eq L^{-1}				
Process	H	Ca	K	SO_4	NO_3
			Dormant Season		
Precipitation	27.87	24.04	2.67	43.56	30.24
Throughfall	27.00	22.72	6.91	41.58	38.44
Stemflow	4.94	158.90	280.52	373.60	9.41
			Growing Season		
Precipitation	42.74	22.79	5.55	69.03	46.92
Throughfall	22.83	44.43	50.24	114.67	53.59
Stemflow	12.64	145.53	269.54	375.53	34.27

Table 2. The 1981 seasonal quantities of elements in precipitation above and below an old-growth sugar maple-yellow birch forest canopy

	Element content, kg ha^{-1}				
Process	H	Ca	K	SO_4-S	NO_3-N
			Dormant Season		
Precipitation	0.17	2.87	0.53	4.02	2.42
Throughfall	0.15	2.44	1.26	3.70	2.88
Stemflow	<0.01	0.05	0.21	0.13	<0.01
			Growing Season		
Precipitation	0.24	2.56	1.21	6.19	3.68
Throughfall	0.11	4.43	9.76	9.14	3.73
Stemflow	<0.01	0.15	0.61	0.37	0.04

Growing Season

Throughfall and stemflow solutions were less acid and richer in bases and SO_4 than was precipitation (Table 1). Quantities of nutrients added to the forest floor within the stand, relative to outside the forest, were smaller for H, larger for Ca, K and SO_4-S, and unchanged for NO_3-N (Table 2).

Annual Budget

Interaction of precipitation with the sugar maple canopy significantly increased (36 to 675%) the annual nutrient addition to soil, in the order of K > SO_4-S> Ca, and decreased (37%) H transfer (Table 3). Throughfall was the major process of element transfer; stemflow, which was 2% of precipitation, contained between 1 and 10% of the total annual deposition of each element in the soil.

DISCUSSION

Precipitation

Variation in nutrient inputs to forest ecosystems is related primarily to fluctuations in precipitation quantity. A total of 1113 mm of precipitation was measured at Watershed 31 in 1981, 559 mm during the growing season, 554 mm during the dormant period. During the same year, 1189 mm of precipitation were recorded at an Atmospheric Environment Service (AES) station, 5 km south of Watershed 31 (Barrie et al. 1982), and 905 mm were recorded at Sault Ste. Marie (Anon 1982a). Mean annual precipitation recorded at the Sault Ste. Marie station is 973 mm (Anon 1982a); hence, 1981 precipitation was 7% below normal.

The Turkey Lakes Watershed is perceived to be within a region of moderate meteoric acid loading and low dry deposition of SO_4-S. In fact, the 1981 mean annual (volume-weighted) pH in bulk precipitation was 4.44 and growing season pH was 4.37. Precipitation at Turkey Lake was less acid

(37 µeq L^{-1}) than in the south and east, e.g., in the New Hampshire-New York area (63 to 83 µeq L^{-1}) (Likens et al. 1977, Cronan 1980, Mollitor and Raynal 1982), but more acid than in the north and west, e.g., in the Minnesota-northern Ontario region (3 to 13 µeq L^{-1}) (White and Kramer 1980, Foster et al. 1984). All three regions are remote from point sources of pollution.

Comparison of Turkey Lakes precipitation chemistry with that at Hubbard Brook Watershed, White Mountains, New Hampshire, and at Huntington Forest, Adirondack Mountains, New York, is of particular interest because throughfall and stemflow chemistry within sugar maple-yellow birch-American beech (*Fagus grandifolia* Ehrh.) forest has been documented at those sites. The 1981 mean annual total molar concentration of cations in precipitation at Turkey Lakes was similar to the 1963 to 1974 mean annual value (Likens et al. 1977), the 1975-1976 mean growing season value in New Hampshire (Cronan 1980), and the 1979 mean growing season value in New York (Mollitor and Raynal 1982). At Turkey Lakes, H accounts for 39% of the cations in precipitation, while in the White and Adirondack mountain regions, H represented 65 to 74% of the total. Precipitation at Turkey Lakes contains 43 µeq L^{-1} of basic cations in comparison with 18 to 21 µeq L^{-1} for the White and Adirondack mountain regions. From an evaluation of precipitation chemistry alone, there would be a greater resistance to soil acidification at Turkey Lakes, because of (a) lower H concentrations and (b) higher base cation concentrations to compete with H for exchange sites in soil, than in the other regions. At all three locations, SO_4 was the dominant anion in precipitation, but its importance, relative to NO_3, was less at Turkey Lakes (SO_4:NO_3, 1.5:1) than in the White and Adirondack mountain regions (2.3 to 3.6:1).

Calcium was the most abundant base in precipitation at Turkey Lakes, followed decreasingly by sodium (Na), K and magnesium (Mg). Annual Ca deposition in bulk precipitation (5.4 kg ha^{-1}) in 1981 was similar to the 5.6 kg ha^{-1} yr^{-1} measured in precipitation 100 km east of the Watershed between 1969 and 1972 (Foster 1974). Differences in Ca concentrations between bulk collectors at watershed 31 (23 µeq L^{-1}) and wet-only samplers at the AES site (11 µeq L^{-1}) (Barrie et al. 1982) suggest that significant dry deposition of alkaline dust occurs at Turkey Lakes.

Table 3. The 1981 annual content of elements in precipitation above and below an old-growth sugar maple-yellow birch forest canopy

	Annual content, kg ha^{-1}				
Process	H	Ca	K	SO_4-S	NO_3-N
Precipitation	0.41	5.43	1.75	10.21	6.10
Throughfall	0.26	6.87	11.02	12.84	6.61
Stemflow	0.01	0.20	0.82	0.51	0.04

Canopy Wash

Annual interception of precipitation by the maple canopy was 5% (9% during the growing season, 1% in the dormant period). Both quantities and relative proportions of the five study elements in precipitation were significantly changed within the forest during the growing season. Atmospheric inputs to soil were reduced 54% for H, increased 65 and 100% for SO_4-S and Ca, respectively, and increased 850% for K by ion exchange and wash-off within the canopy. Relative deposition in soil, outside the forest, was in the order of SO_4-S>NO_3-N>Ca>K>H, and inside the forest it was SO_4-S>K>Ca>NO_3-N>H. In leaf-wash the importance of K increased in relation to NO_3-N, which was not leached from the canopy, and in relation to Ca which was leached but at a lower rate than K.

Approximately half of the precipitation falls during the growing season, when major chemical modification of precipitation by the canopy occurs. Between 75 and 90% of the annual deposition of aqueous K and SO_4-S to the forest floor, and 50 to 60% of the Ca, H and NO_3-N deposition, occur during the leaf-out period.

Stemflow

Stemflow nutrient quantities were derived by using total stocking (all species) and solution volumes and chemical compositions from observations on sugar maple trees only. Applying maple values to all species, however, provides a reasonably good estimate of stemflow element contents since sugar maple comprised 82% of the basal area of the stand.

Stemflow contributed only 3% of the water received by the forest floor during the growing season. Stemflow quantities were somewhat low in relation to the 6% reported for a younger tolerant hardwood forest at Hubbard Brook (Eaton et al. 1973) and the 4 to 6% for other eastern Canadian hardwood species (Mahendrappa 1974), all estimates reported on a growing season basis. As sugar maple trees mature their smooth bark becomes rough, platey and fissured, and hence more resistant to water flow.

Parker (1983), in a review of the role of throughfall and stemflow in the forest nutrient cycle, reported that stemflow contributes between 1 and 20% (an average of 12%) of the flux of nutrients in the water pathway beneath the canopy. Seasonal and annual amounts of elements contained in stemflow in our study were small, despite a high enrichment in K, Ca and SO_4 concentrations in relation to throughfall (3 to 40 times), because of the minimal contribution of stemflow to the flux of water beneath the canopy. Most element transfer took place in the growing season, reflecting greater fluxes of stemflow water (75% of total) in this period (22 events). Drawing conclusions from comparisons of growing season-dormant season element concentrations is not recommended, because stemflow was recorded on only five events in the dormant season. A greater number of events are being studied to examine further how factors such as the time of year, the size, intensity and frequency of storms, and tree size influence stemflow quality and quantity.

Throughfall

Throughfall provided the major pathway for meteoric input of nutrients to soil. Partitioning the nutrients in throughfall that are recycled from vegetation from those that are derived from ecosystem inputs is most difficult. At a given forest site, precipitation chemistry can be altered by canopy filtering (Mayer and Ulrich 1977), canopy uptake (Foster 1974) and internal foliar leaching, acting alone or in combination. In particular, there is a high degree of uncertainty about the importance of dry deposition to throughfall SO_4-S estimates. Diverse sampling methodologies have produced widely different estimates of dry deposition (Parker 1983). Throughfall SO_4-S fluxes in a Norway spruce (*Picea abies* (L.) Karst.) stand exposed to high ambient levels of SO_2 (average 5 to 10 $\mu g\ SO_2\ m^{-3}$ summer, 10 to 20 $\mu g\ m^{-3}$ winter (Mayer and Ulrich 1978)), at Solling, West Germany, were dominated by canopy filtering and dry deposition (Mayer and Ulrich 1977). The leafless sugar maple canopy at Turkey Lakes was not an effective interceptor of S in gases, aerosols or dust, and dry fallout did not increase snowpack SO_4 concentrations within the stand over those observed outside the forest, despite higher SO_2 concentrations in the air during the dormant period (3 to 9 $\mu g\ SO_2\ m^{-3}$ dormant season, 1 to 3 $\mu g\ SO_2\ m^{-3}$ growing season, Barrie et al. 1982). At the moderately polluted Turkey Lakes site, a net removal of 3 $kg\ ha^{-1}$ of SO_4-S from the tolerant hardwood canopy by throughfall during the growing season was observed. If the 3 kg of SO_4-S are from internal foliar leaching, this represents a turnover of one third of the foliar S pool (9 $kg\ ha^{-1}$) (Morrison 1984), and S recycling, via the hydrologic cycle, as great as the annual litterfall additions (3.4 kg ha^{-1}) (Morrison 1984) to the forest floor. More likely, the foliated canopy filters dry deposition of S, and both leaching from within tolerant hardwood foliage and wash-off of dry deposition contribute to the observed moderate enrichment in SO_4-S in throughfall.

A pattern of enrichment in K, Ca and SO_4-S, and depletion in H, in throughfall in comparison with precipitation was observed in tolerant hardwood forests at Turkey Lakes, in the Adirondack Mountains of New York (Mollitor and Raynal 1982) and the White Mountains of New Hampshire (Eaton et al. 1973). Among tolerant hardwood forests, however, there are substantial differences in nutrient leaching from canopies, as well as the differences in nutrient inputs to the ecosystems that have already been discussed. Leaching of K and Ca from forest canopies was decidedly lower at Turkey Lakes than in the other two forests. Likewise, leaching of SO_4-S at Turkey Lakes was lower than in New Hampshire, but higher than in New York. There were differences in base cation leaching from the canopy at Turkey Lakes and Hubbard Brook, New Hampshire, despite similar foliar element concentrations (Eaton et al. 1973, Morrison, unpubl.), similarities in growing season precipitation (Ontario 559 mm, New Hampshire 555 mm) and only small differences in growing season canopy interception of water (9% Ontario, 3% NH). Major differences in the atmospheric inputs of H between the two watersheds might explain observed patterns of base leaching.

According to Tukey (1980), exchange with H ions in precipitation is a means by which the leaching of base cations from within foliage occurs. In the tolerant hardwood forest at Turkey Lakes, 25% of the total cation enrichment below the canopy, during the growing season, could be accounted for by H ion exchange from precipitation. The small decrease in NH_4-N concentration (not shown) in throughfall did not contribute significantly to the amount of ion exchange, which was largely enrichment of bases (K, Ca, Mg, Na) and loss of H. Likewise, in the tolerant hardwood forest in the White Mountains, which has a higher concentration of H, Eaton et al. (1973) reported that 27% of total cation leaching could be explained by proton retention in the canopy. These observations suggest that H exchange contributes significantly to, but does not control, the leaching of cations from hardwood foliage.

Leaching of cations from the canopy increases the rate of cycling of bases between the vegetation and soil and likely enhances the rate of base uptake. There are several reasons for believing that many of the cations will be retained in the ecosystem. In the first place, high infiltration capacity in the forest floor materials ensures that bases in solution will recycle to the tree rooting zone. In the second place, in the Turkey Lakes soil there is considerable cation exchange capacity (10 to 20 meq 100 g^{-1} at pH 7.0) in organic and mineral horizons within the tree rooting zone. In the third place, leaching of cations from the rooting zone occurs infrequently during the growing season.

When plant uptake is inactive during the early spring and late fall periods, however, cation leaching from the rooting zone increases and SO_4 ions contribute significantly to cation transport in the Turkey Lakes soils (Foster et al. 1984). An examination of SO_4- adsorption capacity of the podzolic Turkey Lakes soils indicated low affinities of mineral B horizons for SO_4 (Foster et al. 1984).

The amount of precipitation and the content of total cations were similar at Turkey Lakes and Hubbard Brook (mean elevation 610 m), but meteoric cation input 13 km west of Hubbard Brook at Mount Moosilauke (elev. 1250 m) was much higher because of much greater precipitation (2400 mm) at the latter location. Hydrogen ions made up 39% of the total cation input in precipitation at Turkey Lakes (74% at Hubbard Brook), but only 12% in canopy wash (2% at Hubbard Brook). The amount of H in canopy wash during the growing season (1.15×10^{-8} µeq ha^{-1}) at Turkey Lakes was more than double that at Hubbard Brook (0.46×10^{-8} µeq ha^{-1}). Therefore, lower H input and less modification of H inputs by the canopy were observed at Turkey Lakes than at Hubbard Brook. Inputs of H to tolerant hardwood forest soils are poorly correlated with precipitation H inputs; rather, they are related to site-specific canopy interactions. The lower base content of canopy wash at Turkey Lakes than at Hubbard Brook suggests a greater likelihood of H ion reactions at soil exchange sites and greater possibilities for soil and soil solution acidification. Natural acidity produced in forest floor and mineral soil horizons, however, may be as great as or greater than acidity in canopy wash (Nilsson et al. 1982). Investigations are under way at the Turkey Lakes forest to examine this possibility.

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Heavy Metal Concentration in the Food Chains of Deciduous Forest at Niepolomice, Southern Poland

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ABSTRACT

The Niepolomice Forest (11 000 ha of pine and oak-hornbeam) is situated near the largest steel mill in Poland and the city of Cracow. This forest is thus seriously affected by the emissions from this industrial complex. The concentrations of Cd, Ni, Pb, Cu, Zn, and Fe in the food chain, of oak-hornbeam forests were determined. The following components of the system were analyzed using AAS: higher plants, litter, soil, earthworms, herbivorous invertebrates—Collembola, terrestrial snails, and carnivorous invertebrates—Carabidae. Preliminary results indicate that: litter and soil are the main sinks of heavy metals in the system; the concentrations of some heavy metals increase along the food chain: heavy metal concentrations vary depending on organs and increase with age; contamination of food chains with heavy metals is much higher than in the Bialowieza Forest in northern Poland, the control site; the food chains in the Niepolomice Forest are seriously contaminated by heavy metals when compared to West European and American data for similar forest types.

Time Trends in Selected Chemical Characteristics of Streamflow from an Undisturbed Watershed in West Virginia

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ABSTRACT

Stream chemistry records for a 38.9-ha watershed, undisturbed since 1910, were analyzed for time trends in pH between 1968 and 1982, specific conductance between 1958 and 1982, and calcium, magnesium, potassium, and sodium concentrations between 1970 and 1982. The pH analysis was inconclusive because of an instrument change in 1975, but changes, if they occurred, were very small. There was no change in levels of sodium, potassium, or magnesium, but specific conductance and calcium concentrations have increased slightly in recent years. The cause of these changes is uncertain, but precipitation acidity could be influencing the chemical content of streamflow from this watershed.

INTRODUCTION

One of the major questions about acid rain is whether changes in the chemical characteristics of precipitation, lake water, and stream water have occurred during recent years. Although there is growing evidence of lake acidification in certain areas of North America, conclusions about changing acidity of precipitation or streamflow over time are not well founded because long-term records are scarce.

In this paper we present some chemical characteristics of a second-order stream draining a forested watershed from 1958 through 1982. Chemical characteristics of precipitation from July 1978 through September 1982 are presented to document the recent acid load in precipitation.

Streamflow data are from a 39-ha watershed on the Fernow Experimental Forest near Parsons, West Virginia, at latitude 39° 03' N and longitude 79° 38' W. Elevation of the study watershed ranges from 560 to 640 m above sea level. The soil type is predominately Calvin silt loam (USDA Soil Conservation Service 1970), with bedrock of fractured sandstone and shale. Soil depth ranges from 90 to 150 cm, and the average soil pH is about 4.5.

This watershed has not been disturbed by forest harvest or grazing since 1910, when most of the merchantable timber was removed. Vegetation is mixed hardwoods, including yellow-poplar, *Liriodendron tulipifera* L.; sugar maple, *Acer saccharum* Marsh.; black cherry, *Prunus serotina* Ehrh.; white ash, *Fraxinus americana* L.; basswood, *Tilia americana* L.; northern red oak, *Quercus rubra* L.; and hickory, *Carya* spp. American chestnut, *Castanea dentata* (Marsh.) Bork., was a major forest component until it was killed by the chestnut blight *Endothia parasitica* in the 1930s.

MATERIALS AND METHODS

Streamflow was measured with a 120° V-notch weir. Between 1958 and 1966, pH was determined in the field above the weir with a Hellige color indicator kit.[1] Beginning in 1968, water samples were brought to the laboratory and refrigerated within 2 hours after collection. A Leeds and Northrup electrical meter was used to determine pH between 1968 and 1975; a Corning Model 10 meter has been used since 1976. The meters were carefully calibrated with pH 4.0 and 7.0 buffer solutions before each set of readings, which were made within 24 hours after collection. Specific conductance was measured with a Beckman Solu-bridge meter from 1958 to the present. The four major cations, Ca^{2+}, Mg^{2+}, K^+, Na^+, have been determined by the atomic absorption method since 1970.

Stream pH data were first converted to hydrogen ion concentration and these values tested by simple regression for correlation with flow rate at the time of collection. Next, H^+ values were averaged for the following time periods: annual, February-April, May-July, August-October, and November-January. Finally, each average H^+ was converted back to pH and a simple regression run for each time period. Average pH and calendar year were the dependent and independent variables respectively. Since flows usually are greatest from February to April, chances for showing a pH time trend may be greater at this time than in late summer and autumn when average flows are at a minimum.

Specific conductance and individual cation concentration, were averaged arithmetically for each year, plotted for the period of record, and tested for a time trend as described for pH.

Wet precipitation was collected with an automatic sampler beginning in July 1978. From that time, weekly precipitation was collected and subsamples analyzed locally for pH and specific conductance. The remaining samples were sent to the Central Analytical Laboratory in Champaign, Illinois, where pH, conductance, and Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, and PO_4^{3-} concentrations were determined.

Precipitation data were analyzed by (1) converting each weekly pH value to hydrogen ion concentration and weighting according to weekly precipitation volume, (2) averaging these weighted values by calendar months, and (3) converting back to pH units. These monthly values were plotted to show seasonal trends. Average monthly SO_4^{2-}, NO_3^-, and Cl^- concentrations were correlated with average monthly H^+ concentrations.

RESULTS

Precipitation Chemistry

Although the precipitation records cover only a 54-month period, they indicate a seasonal cycle of SO_4^{2-} and H^+, whereas NO_3^- is not as seasonally dependent (Fig. 1). The average annual pH was 4.15. The annual range of H^+ is 39 μeq L^{-1} (pH 4.40) in December to 96.7 μeq L^{-1} (pH 4.02) in August. Simple correlation (r) of monthly H^+ with SO_4^{2-} and NO_3^- was 0.95 and 0.70 respectively. Chlorine concentration was not significantly correlated with H^+ ($r = 0.13$). The average ∫ mg L^{-1} ratio of SO_4^{2-} to NO_3^- was 1.89 and ranged from 1.42 in January to 2.40 in August. Average annual loading of SO_4^{2-} to NO_3^- was 46.2 and 24.3 kg ha^{-1} respectively.

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[1] The use of trade, firm, or corporation names in this publication is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture or the Forest Service of any product or service to the exclusion of others that may be suitable.

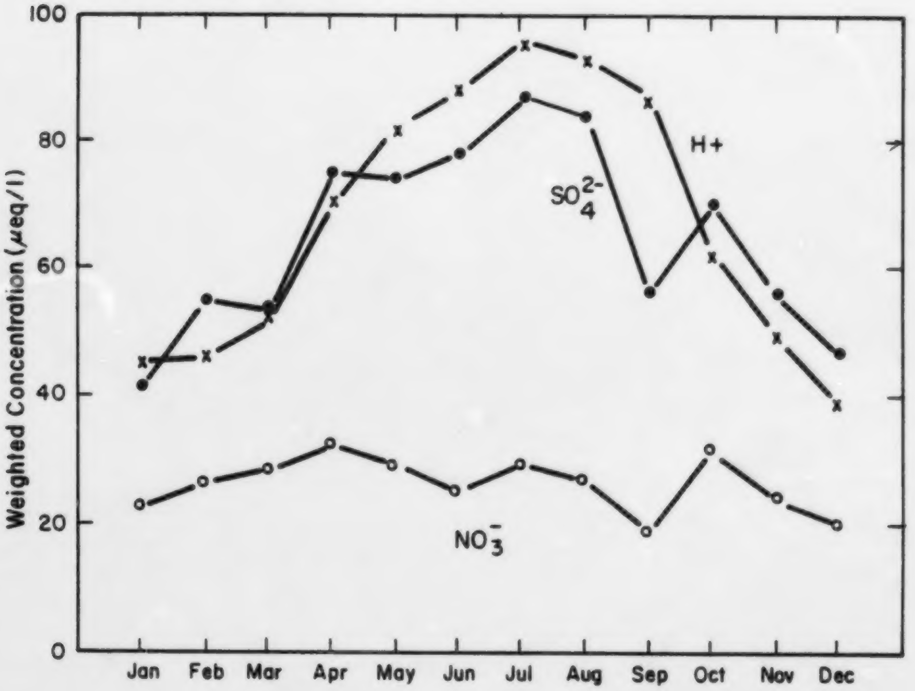

Figure 1. Average monthly concentration of NO_3^-, SO_4^{2-}, and H^+ in precipitation at Parsons, West Virginia, from July 1978 through December 1982.

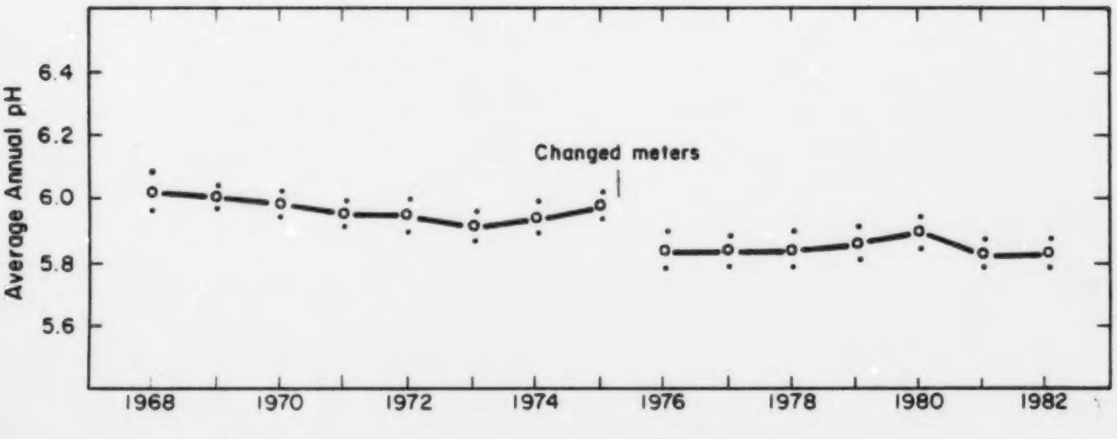

Figure 2. Average annual pH with 95% confidence interval.

Stream Water Chemistry

Streamflow pH was not significantly related to concurrent flow rate, though there were decreases of as much as 0.20 unit during individual storms. A frequency distribution of discharge rate by flow classes and the corresponding pH value indicated that the most frequent pH in all flow classes was 5.90. Flow rates ranged from 0.20 to more than 140 litres per second. Because pH records obtained with the Hellige kit fluctuated too much from year to year for a meaningful time-trend analysis, only records from 1968 to 1982 are presented (Fig. 2).

A regression analysis for the period 1968-75, when the Leeds and Northrup meter was used, indicated that pH decreased by 0.007 unit per year on average, but the coefficient of determination (R^2) was only 0.25 and the regression was not significant at the 0.05 probability level.

The marked drop in mean annual pH between 1975 and 1976 probably is related to the change in meters; unfortunately, no comparison readings were made before the Corning meter was accepted as a standard instrument. A regression indicated no significant change in mean pH between 1976 and 1982. We conclude that if average annual pH of streamflow from this watershed has changed significantly, we are unable to show the change because of technological improvements and methodological changes.

Results of the seasonal averages did not differ significantly from the annual values. The regression slope coefficients for early spring and late summer averages were the same (-0.006 pH unit per year), but the R^2 values were 0.20 and 0.05 for early spring and late summer, respectively. We conclude from this analysis that seasonal as well as annual averages show no trend in pH over time.

Figure 3 shows average annual specific conductance with a 95% confidence interval during the period 1958-82. A change in analytical instruments was made in 1973, but extensive tests indicated no significant difference between meters. From 1958 to 1968, conductance decreased slightly, but there has been a steady increase since 1968.

Although there is no indication of changing concentrations of Mg^{2+}, K^+, or Na^+ in stream water with time, the concentration of Ca^{2+} appears to increase between 1970 and 1982 (Fig. 4). A seasonal analysis indicated an increasing trend for periods of high flow (February-April), but no detectable change for late summer.

DISCUSSION

The seasonal cycle of H^+ and SO_4^{2-} illustrated in Figure 1 has been observed at other locations in the eastern United States (Hornbeck et al. 1976; Likens et al. 1977). The reason for the cycle has not been firmly established but it may be related to seasonal variations in air trajectories and/or to air stagnation in summer months. Winter storms are accompanied by higher wind speeds with a westerly component, whereas summer rains are associated with weaker movement of air masses and lighter winds from the south (Trent et al. 1970). Fisher et al. (1968) reasoned that snow was less efficient in capturing sulfur compounds than liquid precipitation. Hornbeck et al. (1976) suggested that electric power production by midwestern utilities may be greater in summer than in winter, which would indicate more coal combustion and possibly more atmospheric pollution during the summer months.

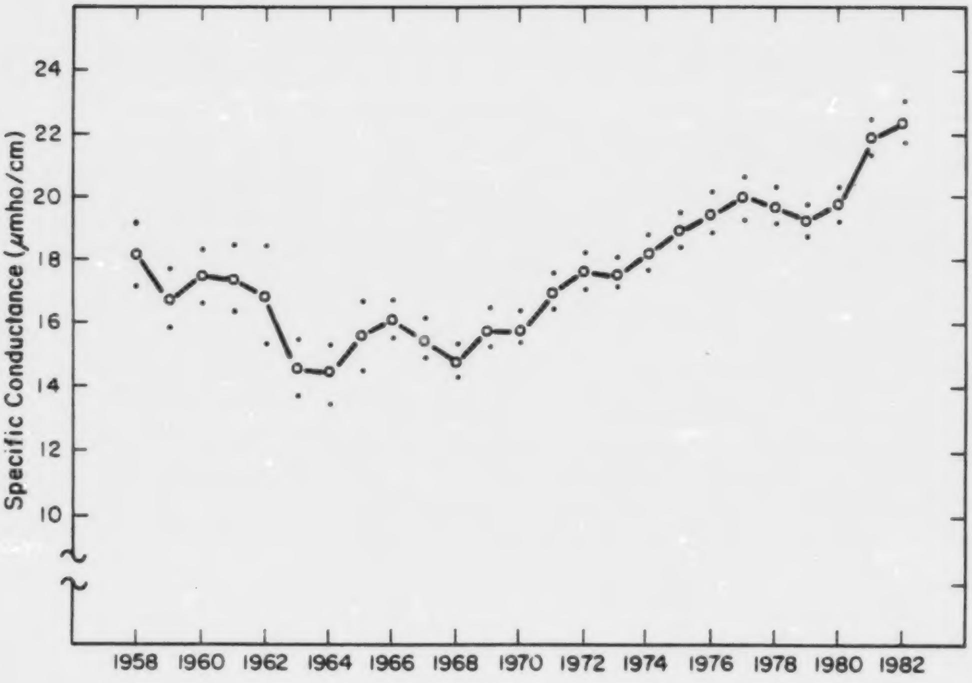

Figure 3. Average annual specific conductance with 95% confidence interval.

Figure 2 could be interpreted as indicating a decrease in stream pH if instrument changes were not considered. This figure reinforces the conclusions of Hornbeck (1981): "Finding the pH of precipitation is not the simple, easy determination that most foresters are familiar with from their college soils and chemistry courses." Hornbeck listed sample temperature, stirring time, types of electrodes, and strength of calibrating buffers as possibly affecting the final reading. Although it is impossible to know the accuracy of historical records, part of the within-year variation and the apparent drop in pH in 1976 (Fig. 2) are probably related to laboratory techniques and instrument change.

Contrary to much speculation about stream acidification in the Appalachian Mountains (e.g., Collins 1981), we could find no concrete evidence that acidity of Appalachian streams has increased during recent years. An analysis of 12 years of pH data from the Shavers Fork River in West Virginia showed seasonal cycles in pH, presumably associated with flow rates, but no time trends. It was concluded that measurement precision (± 0.20 pH unit) masked any change that might be expected.[2] At other locations in the East, Johnson (1979) presented the strongest evidence that we could find that streams have become more acidic. He analyzed 17 years of chemistry data from two small streams in the New Jersey Pine Barrens and found a total pH decline of about 0.40 unit. He concluded: "Acidification of streams in the Pine Barrens is probably a real phenomenon. There appears to be no bias due to sampling or analysis."

Since no fertilizer has been added to our watershed and no timber has been harvested during the past 50 years, the increase in specific conductance since 1958 (Fig. 3) and the apparent increase in calcium concentration (Fig. 4) could be related to atmospheric deposition. Others (e.g., Jonsson and Sunberg 1972; Cronan 1980) suspect that acid precipitation leaches mineral bases from soils and will eventually cause a loss of productivity.

We believe that the watershed is potentially very sensitive to stream acidification and nutrient leaching by atmospheric deposition. Average soil pH is about 4.5, stream pH is only slightly acidic, and natural stream alkalinity averages only 0.75 mg L^{-1} as $CaCO_3$. The acid load is greater than in many areas of the Appalachians because of abundant precipitation (140 cm yr^{-1}) and low pH (about 4.15). Although the forest canopy, soil profile, and bedrock are currently effective in neutralizing acids received in precipitation, we do not know the limits of these systems. Therefore, we will continue monitoring streamflow chemistry to better define trends in each chemical parameter over time. Extra precautions were initiated in 1980 to improve quality control of chemical analysis so that local results are comparable with results from other laboratories.

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[2] Dunshie, Dale. 1979. Evaluation of the surface water resources of the Shavers Fork River. Unpublished report on file, Monongahela National Forest, Elkins, West Virginia.

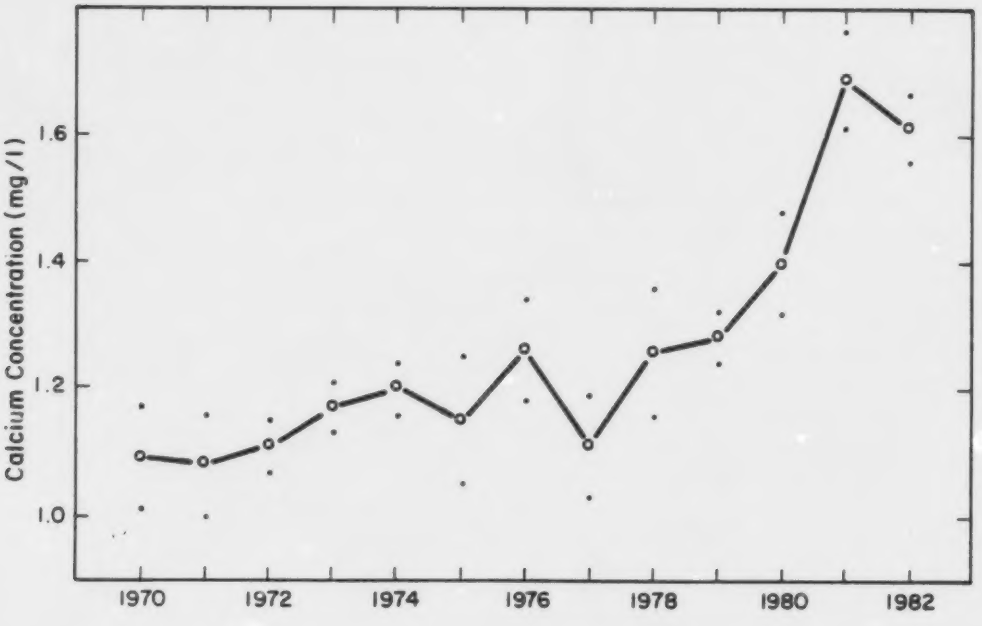

Figure 4. Average annual calcium concentration with 95% confidence interval.

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Distribution of Airborne Pollutants Within a Forest System: Effects of Metal and Sulfur Dioxide Deposition on Vegetation and Soils

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ABSTRACT

Metal and sulfur deposition from a nickel-copper smelter onto a boreal forest system was investigated. Elevated levels of nickel and copper were found in vegetation and soils up to 20 km from the source. Metal-contaminated soils from sites close to the source ($<$ 2.5 km) contained over 1500 mg kg^{-1} Ni and 300 mg kg^{-1} Cu, which significantly impaired the growth of jack pine (*Pinus banksiana* Lamb.) seedlings. Seedling chlorosis and root morphology of greenhouse-grown plants indicated that metal toxicity was the cause of reduced seedling growth.

Elevated sulfur levels were found in needles of black spruce (*Picea mariana* L.) from the field sites, but were not found in jack pine foliage or soils taken from the same locations. Surface soil pH ranged from 3.4 to 5.6 but was not related to distance from the source, indicating that soil acidification had not taken place as a result of high SO_2 emission rates ($>$ 1000 t day^{-1}). The combined effects of metal particulates and sulfur dioxide were not sufficient to bring about changes in seed quality or foliar nutrient composition.

Forest Soil Acidification in Southern Finland

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ABSTRACT

Increasing acidity of precipitation and increased dry deposition of acidifying substances have been observed in southern Finland. The Uusimaa forest districts have been divided and mapped as four different sulphur-deposition classes according to needle sulphur contents. Forest soil samples were collected from the deposition areas studied, and the hydrogen-ion concentration, conductivity and amounts of exchangeable Al^{3+} determined. The soil samples were taken from the humus layers (surface humus layer A_0 and bottom humus layer $A_1 + A_2$) and from the soil at a depth of 0.3 - 0.5 m (B or C).

Some regional features of soil-humus acidity were found around higher deposition areas; the mean pH of humus samples was $<$ pH 4.15 or from pH 4.16 to 4.35. The normal mean pH of southern Finnish *Calluna* type forests is from pH 4.36 to 4.55. Some areas with better buffered clay have pH $>$ 4.56. A slight acidification of the poorer forest types can be indicated on the basis of older soil analyses from the 1950s. The solubility of soil aluminum increases below pH 4.5. Some indication of increased solubility was found in areas with increased acidification.

Composition of Throughfall from Variable Forest Cover Types Exposed to Acid Rain in Central New Brunswick

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ABSTRACT

Throughfall under deciduous, coniferous and mixed forest cover was captured by 25 fixed collectors on each of three 0.25-ha plots from April through October in 1981 and 1982. Incident precipitation was sampled from a bulk-deposition collector located in a nearby clearing. Throughfall pH was generally higher than that of ambient precipitation; deciduous, coniferous and mixed forest cover removed 77, 76 and 80% of H^+ ions, respectively. Concentrations of organic N, total P, K^+, Ca^{2+} and Mg^{2+} in throughfall were greater than the corresponding concentrations of precipitation at all sampling dates. No less than 85% of throughfall samples analysed exhibited increased concentration of Na^+, SO_4^{2-} and total N. Contents of inorganic N were usually lower in throughfall than in incident precipitation. The sum of cations (equivalents of Na^+, K^+, Ca^{2+} and Mg^{2+} ha^{-1}), and particularly the individual amounts of Ca^{2+} and Mg^{2+} leached from the canopy during a given sampling period, were closely correlated ($r > 0.8$) with the removal of H^+ (equivalents ha^{-1}) by the canopy from the incident precipitation. This substantiates earlier suggestions that leaching of nutrient cations from the canopy involves an ion-exchange process.

Chemical Characteristics of Sequential Acid-Rain Episodes, Canopy Throughfall and Streamwater Quality in a Yellow Birch Stand, Laurentides Park, Canada

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ABSTRACT

Sequential sampling of incident precipitation (rain), throughfall and streamwaters during individual storm events in a mature yellow birch watershed (Lake Tantaré, Laurentides Park region, Québec) showed that the effect of the tree cover on the precipitation caused the resultant throughfall to reflect chemical characteristics related to dry deposition washoff and leaching of the vegetative canopy. Total canopy net exchange (deposition ratio) of soluble components ($<0.45\ \mu m$) with the incident precipitation increased in the order of $Pb < H^+ < Al < Na^+ < SO_4^{2-} < Fe < NO_3^- < Ca^{2+} < Mg^{2+} < Mn < K^+$. The rate of dry deposition washoff was best estimated from Al and Fe analysis of sequential samples, which in turn permitted the determination of the net leaching rates of elements where total deposition ratios were high (Ca, Mg, Mn and K). Marked differences between throughfall chemical characteristics of different events (e.g. pH) were not reflected by the major headwater streams (pH 4.4-4.8) draining the watershed. Al, present in only low concentrations in both precipitation and throughfall, is found to be constantly present at high concentrations in the streamwaters.

INTRODUCTION

The progressive increase in acid precipitation over large areas of eastern North America due to the long-range transport of atmospheric pollutants (Likens and Butler 1981; Ouellet and Jones 1982) has been cited as the factor responsible for the rise in the acidity levels of aquatic ecosystems (Burns et al. 1981) and is also suspected of being a major factor in the decline of eastern forests within the last two decades (Johnson and Siccama 1983). This decline is characterized by the dieback and excessive mortality of trees (e.g. red spruce), particularly at high elevations, where physical interaction between cloud cover and vegetation occurs frequently. Interaction between tree canopies and rain at lower elevations results in chemical modification of the latter both by dry deposition washoff from the leaves, branches and stems and by leaching from leaves. The evidence for the negative impact of foliar leaching by present levels of acid rain on forest growth is thought not to be significant relative to that for the negative impacts on the soil/root matrix (Johnson and Siccama 1983). However, these conclusions are based mostly on short-term experimental observations of visual foliar damage under extreme acid treatment (pH <3) (Wood and Bormann 1975) and cannot be directly applied to forests such as those in the northeastern areas of America which have been exposed for decades to atmospheric pollutants. In this particular context progressive physiological weakening of tree functions could be the result of the increased energetic demands imposed on tree translocation mechanisms for the accelerated transport of essential nutrients during acid-induced stress. This would be a response to micro-lesions caused by impacted and absorbed acidic aerosols and the compensation required for nutrient loss due to leaching from leaf intercellular spaces by dissolution of metabolites or neutralization of hydrogen ions (Parker 1983). As noted above (Wood and Bormann 1975), however, lesions of tree foliage due to atmospheric aerosols which give rise to precipitation pH values of from 4.2 to 4.5 do not seem to produce outward visible lesions in leaf cuticles. The major stress of acidic precipitation on the canopy of northeastern forests could thus be the leaching of nutrients from the interior of the leaf structure. The relationship between this phenomenon and the impact of acidic precipitation on the soil/root matrix would be synergetic with the dependence of canopy transport on the latter. These implications of the differences between the effects of dry deposition and leaching on tree metabolism have led many authors to attempt to differentiate both phenomena or one or the other by either direct or indirect means (Parker 1983). One such indirect method is the determination of the contribution of dry deposition washoff to total throughfall deposition; subsequent comparison of the latter with the deposition of the incident precipitation should then permit an estimation of the leaching rate of certain nutrients from the tree canopy. In this paper we report the results of an attempt by indirect means, i.e. the chemical analysis of sequential rain samples during discrete events (spring-fall 1982), to establish the contribution of canopy leaching to throughfall quality in a mature yellow birch stand in the Laurentides mixed forest in eastern Canada. In addition, concomitant measurements on streamwater quality were carried out to ascertain if any global repercussions on surface water quality could be related to throughfall characteristics during individual events.

SITE SPECIFICATIONS

The site chosen for the study was a mature yellow birch stand on the eastern shoreline of Lake Tantaré (0.99 km^2, watershed 10 km^2) 40 km north of Québec City, Canada (Ouellet and Jones 1983). The watershed has never been settled or exploited except for two minor experimental logging operations in the 1940s and 1960s. The lake and watershed are designated the Tantaré ecological reserve and are managed by the Québec government. Within the reserve certain experimental programs may be carried out. There are no appreciable point sources of acidic pollutants within a 50-km radius and the only possible source of any short-range atmospheric particulate input would be the Canadian Armed Forces Defense Research establishment at the Valcartier Base 10 km to the southwest. Precipitation in this area is 1100 mm yr^{-1}, of which about 30% falls as snow; the present mean acidity level is pH 4.2. Soil cover (podzols) on the watershed is thin and overlies gneiss and granitic bedrock; at higher elevations glacial tell is mostly absent. In seasons with prolonged dry periods streamflow becomes intermittent and responds rapidly to appreciable amounts of precipitation. Stream acidity is consistently high (pH $\simeq$ 4.6, [H$^+$] = 25.1 µeq L^{-1}) for all main streams with rock beds; small streams with hypodermic flow show lower acidity values (pH $\simeq$ 6.0, [H$^+$] $\simeq$ 1 µeq L^{-1}). Lake pH values vary from 4.9 to 5.2; the changes in lake community structure in the past decade, i.e. macrophyte colonisation, increased transparency and regression of the natural trout population, have led to the suggestion that this lake is undergoing the acidification process so well described for lakes in other regions (Wright et al. 1980).

METHODS

A precipitation sampler was constructed by nailing a convoluted fiberglass sheet (1 m x 2 m) on a wood frame; the heads of the nails were subsequently surrounded by plastic to prevent metal contamination. The frame was set at a slight angle to the horizontal so that intercepted precipitation flowed into a plastic gutter collector with attached bottles. The sampler was placed under a large mature yellow birch tree ($\simeq$ 100-150 years old) in a well-spaced stand with complete canopy cover. A similar sampler was placed in a clearing (20 m from the birch tree) with no canopy interception within a radius of 15 m of the sampler. Both samplers collectors and bottles were washed with nitric acid (0.5 mL HNO_3 (40%); 1 L distilled water) and well rinsed with distilled water in dry periods. After preparation of the samplers and before the onset of an event, the samplers and collectors were covered with convoluted fiberglass sheets to eliminate any dry deposition accumulation and subsequent contamination of the incident precipitation or throughfall. Streamwaters were sampled directly at the gauging station on the stream 850 m from the throughfall sampler. At the onset of an event, both precipitation samplers and stream sampler operators using synchronized chronometers noted the volume collected v time, or stream level v time, relationships as the event progressed. Samples were prefiltered through a 177-µm plastic grid and pH and conductivity were measured by means of a specific-ion electrode (radiometer PHM53) and conductivity meter (radiometer CDM) immediately following the event. The samples were further filtered (millipore 0.45-µm filter), kept cold (0-4°C) and the anions (Cl^-, PO_4^{3-}, SO_4^{2-}, NO_3^-) analyzed by ion chromatography within 48 hours of sampling. Analyses for major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and metals (Fe, Al, Ca, Mn, Cr, Pb) were carried out by atomic absorption within the prescribed limit of 6 months on samples preserved with nitric acid solution (Jones and Bisson 1980).

RESULTS AND DISCUSSION

Rain Events

Sequential sampling events were carried out on four separate occasions (June 29, July 28, August 19 and September 27) during the spring to fall period 1982, during which the yellow birch stand went from a full spring-leaf condition to the canopy-senescent stage just before litter fall. Figures 1 and 2 show the precipitation rates of each event at the time of sampling. The continuous and fairly steady rainfall of June 29 was sampled in its entirety over a period of approximately 1.5 hours. By contrast, the event of July 28, a torrential downpour, was sampled every 20 seconds after the onset of the event, up to 10 minutes, at which time the operation was discontinued. The precipitation rate during the rainfall of August 19 was irregular and fluctuated from fine misty rain to more intense rate episodes; this event was sequentially sampled over a period of approximately 1.5 hours at which time the event tailed off as a fine mist. The last event, September 9, represented a day-long period of intermittent rain on which sequential sampling was carried out for a period of 1.5 hours of continuous light rain. This occurred 6 hours after the first of the many intermittent rain periods was recorded. Integration of the respective rates to give the total rain water deposition measured during each event (Table 1) showed that interception and/or evaporation of the incident precipitation was only of consequence in the light rain of August 19 when 42% of the latter was retained by the canopy.

Total Ionic and Metal Deposition

To eliminate concentration effects due to canopy evaporation of the incident precipitation, in a comparison between the chemical composition of the latter and that of the throughfall, total depositions of the major ionic species (μeq m^{-2}) and metals (μg m^{-2}) were calculated for the period of time required to collect each individual sample. The summation of these individual deposition quantities then gave values for the total deposition of major ions and metals that occurred during the entirety of each of the four rainfall episodes (Table 1).

A comparison between the total quantity of major ions (μeq m^{-2}) and heavy metals (μg m^{-2}) deposited by the incident rainfall during each event shows that most of the incident rains contained relatively small quantities of soluble impurities; the rainfall of August 19, however, is remarkable for the high content of all ions and heavy metals.

Mean deposition ratios (D_C/D_I : D_C, canopy throughfall deposition; D_I, incident rain deposition) for all events were Pb (0.6 ± 0.2) $<H^+$ (0.74 ± 0.83) $<$Al (1.5 ± 1.0) $<Na^+$ (1.7 ± 0.4) $<SO_4^{2-}$ (1.8 ± 0.7) $<$Fe (2.8 ± 2.2) $<NO_3^-$ (9.5 ± 11.9) $<Ca^{2+}$ (11.3 ± 12.0) $<Mg^{2+}$ (24.6 ± 21.6) $<$Mn (43.1 ± 43.7) $<K^+$ (67.5 ± 69.9). These values compare relatively well to those calculated from the data of Eaton et al. (1987) for a yellow birch stand in New Hampshire (H^+, 0.06; Na^+, 1.7; NO_3^-, 2.8; SO_4^{2-}, 3.9; Ca^{2+}, 9.4; Mg^{2+}, 18.7; K^+, 72.0) during a similar period (June-October). The low values for Pb, Al, Na^+, SO_4^{2-} and Fe reflect the small amounts of these materials that the canopy contributes to the throughfall. This indicates that in this particular experimental situation the major additional source of these elements in precipitation after canopy contact is washoff of dry deposition. Na^+, Al and Fe thus contribute little to the buffering capacity of the canopy which relies mainly on the leaching of such elements as Ca^{2+}, Mg^{2+}, Mn and K^+ with high deposition ratios. There is, however, no direct relationship between buffering capacity of the canopy at any one time and the concomitant leaching of Ca^{2+}, Mg^{2+}, Mn and K^+. Figure 3, showing the net loss or gain of H^+, Mg^{2+}, K^+ and Na^+ (μeq mm^{-1} m^{-2})

Table 1. Physical and chemical characteristics of incident precipitation (0) and throughfall (C) for four rain events, Lake Tantaré, Québec, 1982.

			Total Deposition																									
Event	Duration (min)		Precipitation (mm)		H^+ µeq m⁻²		Ca^{2+} µeq m⁻²		Mg^{2+} µeq m⁻²		K^+ µeq m⁻²		Na^+ µeq m⁻²		Fe µeq m⁻²		Mn µeq m⁻²		Al µeq m⁻²		Pb µeq m⁻²		NO_3 µeq m⁻²		SO_4 µeq m⁻²			
	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C		
29-06	96.0	108.0	5.01	4.82	82.8	4.7	2.5	68.8	1.6	80.5	1.9	117.2	21.3	44.1	31.5	163.6	5.0	186.0	19.5	47.9	16.1	9.0						
28-07	10.0	10.0	13.45	13.45	494.0	225.0	83.0	296.3	28.2	343.9	30.6	431.4	31.6	46.0	703.0	1101.0	62.0	908.0	519.0	719.0	71.6	51.8	99.7*	233.2*	104.7*	180.9*		
19-08	168.0	170.0	5.36	3.14	113.8	54.6	456.4	444.7	65.5	148.5	28.0	237.8	22.4	28.1	1126.5	350.7	70.9	984.7	1026.6	216.0	37.5	12.2	286.2	207.9	289.5	345.7		
27-09**	124.0	145.0	2.69	2.69	82.2	159.3	15.0	196.2	2.3	78.6	1.2	186.9	3.6	6.4	13.5	55.7	6.1	650.2	5.1	9.1	10.0	6.8	51.5	253.0	87.8	224.7		

* total deposition up to 6 minutes only

** sequential sampling period started 6 hours after start of intermittent rain

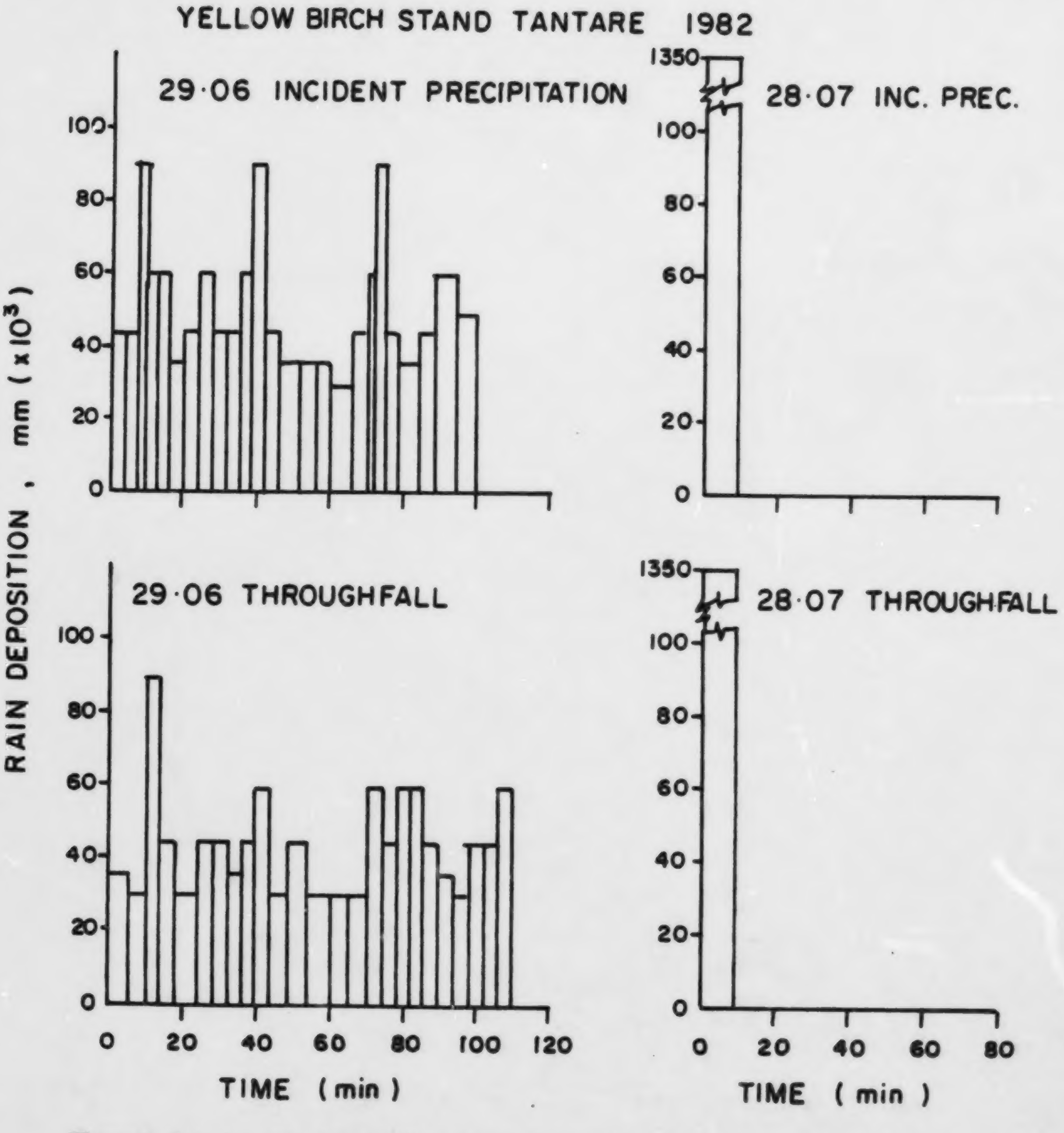

Figure 1. Rain deposition (mm x 10^3), yellow birch stand, Tantaré, June 29 and July 28, 1982.

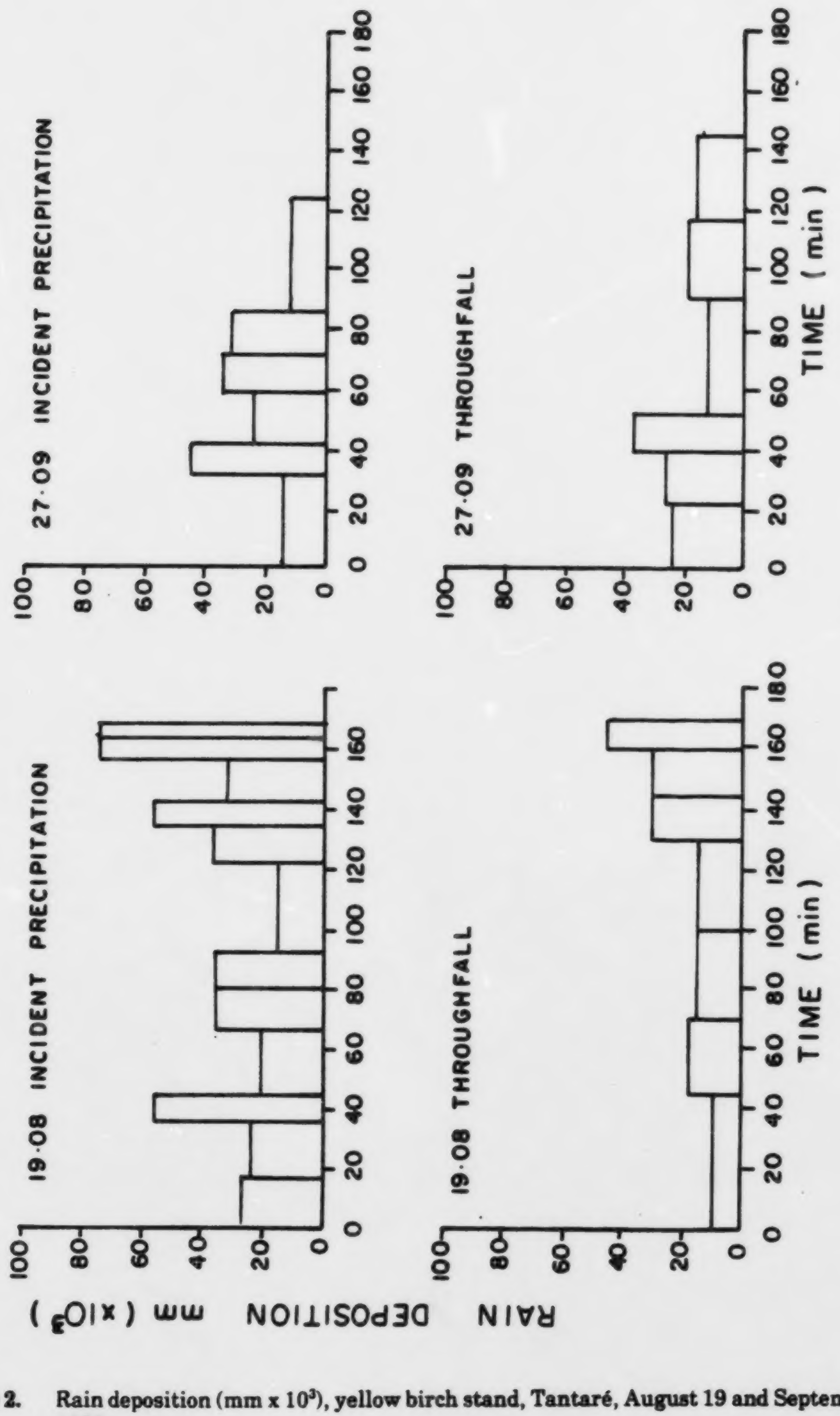

Figure 2. Rain deposition (mm x 10^3), yellow birch stand, Tantaré, August 19 and September 27, 1982.

by the incident rainfall after canopy contact (throughfall) for the four events studied, demonstrates that leaching from the canopy is far in excess of that required for the neutralization of the H^+ concentration in the incident precipitation. In addition, the leaching rates which increase during the late summer and fall season can also register high values without contributing to any net neutralization of the incident precipitation (e.g. the rain event of 27-09). It seems that this leaching process of major cations from the canopy is associated primarily with the removal of organic material (Hoffmann et al. 1980). This is indicated by both the high organic content of throughfall compared to that of incident precipitation and the relatively large anionic deficiencies that are shown by the former vis-à-vis the latter when ionic balances for the two types of precipitation are compared (e.g. for the event of September 21: Σ-ve = 1.42 Σ+ve - 1.34, $r^2 = 0.93$, n = 7 for incident precipitation; Σ-ve = 1.37 Σ+ve - 60.25, $r^2 = 0.99$, n = 7 for canopy throughfall where Σ -ve = sum of major anions Cl^-, PO_4^{3-}, NO_3^-, SO_4^{2-} and Σ+ve = sum of major cations H^+, Ca^{2+}, Mg^{2+}, K^+ and Na^+).

Sequential Ionic and Metal Deposition Rates

From a consideration of the deposition ratios (D_C/D_I) for the various major ions and metals studied, an attempt was made to use the sequential sample analysis of throughfall for Fe, Al, SO_4^{2} and Na^+ as indicators of dry deposition washoff rate. In this area, incident precipitation, either as rain or as snow (Jones and Bisson 1980), occasionally contains high loadings of Fe and Al that are significantly correlated (Al = 0.96 x Fe - 3.72 $\mu g\,m^{-2}$, $r^2 = 0.96$, n = 60 for incident precipitation, spring-fall 1982). The relative amounts of these elements in throughfall for the same period are also strongly correlated (Al = 0.8 x Fe -1.90 $\mu g\,m^{-2}$, $r^2 = 0.92$, n = 65). Although the origin of this atmospheric loading is not precisely known it is probably the result of short-range transport of large dust particles as the deposition rate of these materials may fluctuate greatly during the same event. In some conditions, e.g. those prevalent during the event of August 19, the canopy may even show an apparent uptake of Fe and Al (Table 1). However, in circumstances combining constant low loadings of Fe and Al in the incident precipitation with a steady rate of rainfall, sequential analysis of these elements in both throughfall and the incident precipitation can lead to an estimation of the rate of washoff of dry deposition. Figures 4 and 5, which reproduce the Fe and Al deposition rates for the July 28 event, show that the rate of washoff of dry deposition by throughfall followed an exponential trend typical of a first-order reaction and reached the asymptotic value of the background precipitation Fe and Al loadings 6 min (8.1 mm rain) after the event had started. This also corresponds closely to the time taken for the SO_4^{2-} deposition rate in the throughfall to attain that of the incident precipitation (Fig. 6) but not that of Na^+ (Fig. 7). The throughfall deposition rate of this last ion dropped off rapidly to that of the incident precipitation within 1 min (1.35 mm) after the onset of the event. This is probably related to the differing rates of solubilisation or detachment of the dry deposition which in turn depend on the nature of the deposed material (Little 1977).

Lead, Cu and Cr proved to be poor indicators of dry deposition washoff; Cu and Cr were constantly near the detection limits of the methods used, Pb quantities were lower in throughfall than in the incident precipitation and no clear trends in washoff were observed. This is expected as the soluble forms of lead aerosols impacted on forest canopies are present in far lower concentrations than those found in incident precipitations (Lindberg and Harriss 1981).

The exponential fall-off in elements of low deposition ratios was also observed during the sequential sampling of the event of September 27. It was further observed, but to a lesser extent, during the event of June 29; this was due to periodic fluctuations in the concentrations of Fe and Al during the event. In the case of the event of August 19 when the rain was very heavily loaded with mineral matter, Fe and Al values increased five-fold during the event and the chemical characteristics of the throughfall followed closely the concomitant changes in the incident precipitation. Sequential chemical patterns in individual events (Yawney and Leaf 1971; Sollins and Drewry 1970) are thus dependent on both canopy loadings of dry deposited materials and potential leachates and the variation in the quantities of the same materials in the incident rainfall during the event.

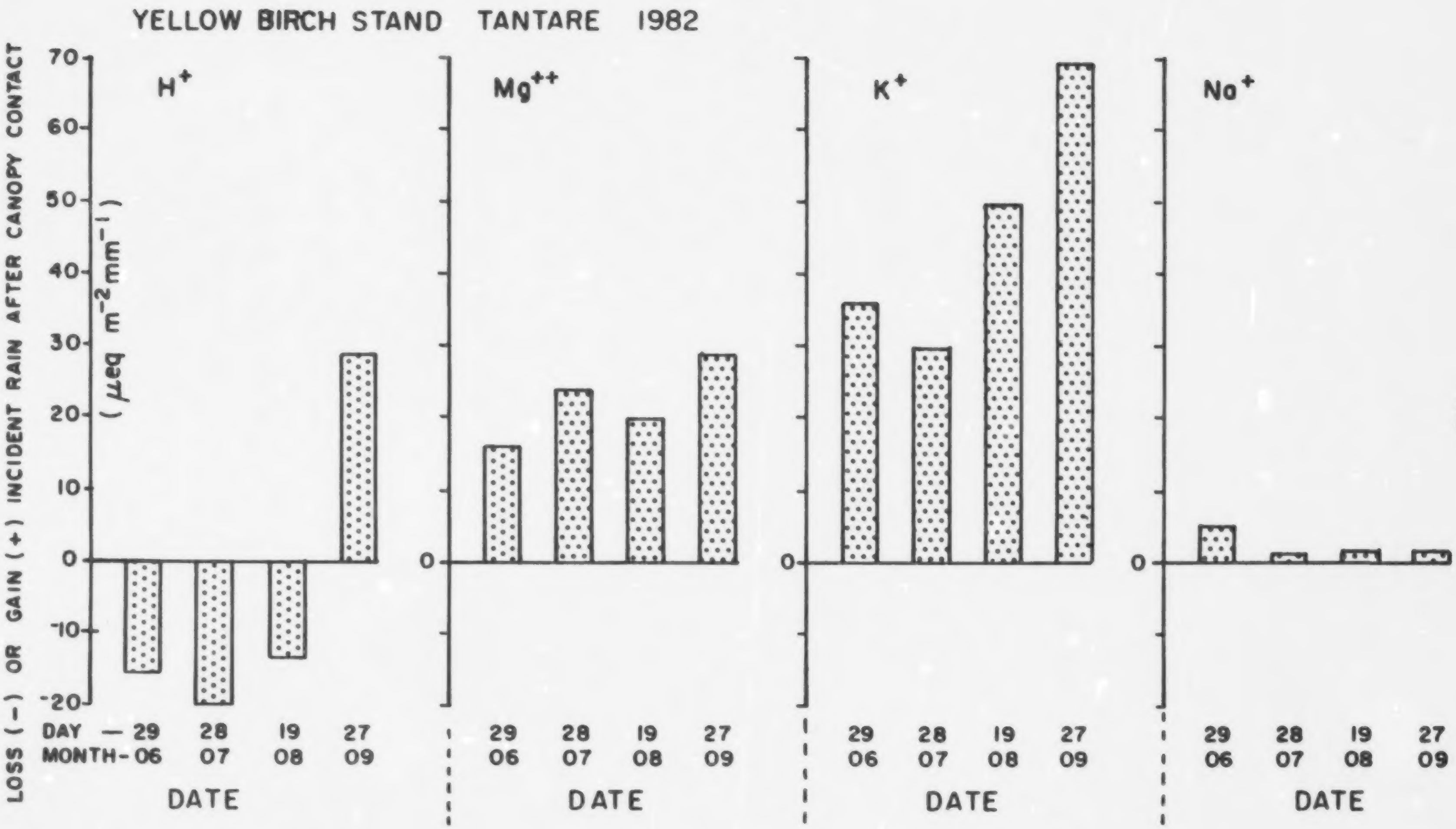

Figure 3. Loss (-) or gain (+) of H$^+$, Mg^{2+}, K$^+$ and Na$^+$ (μeq m-2mm-1) by the incident rainfall after canopy contact, yellow birch stand, Tantaré, 1982.

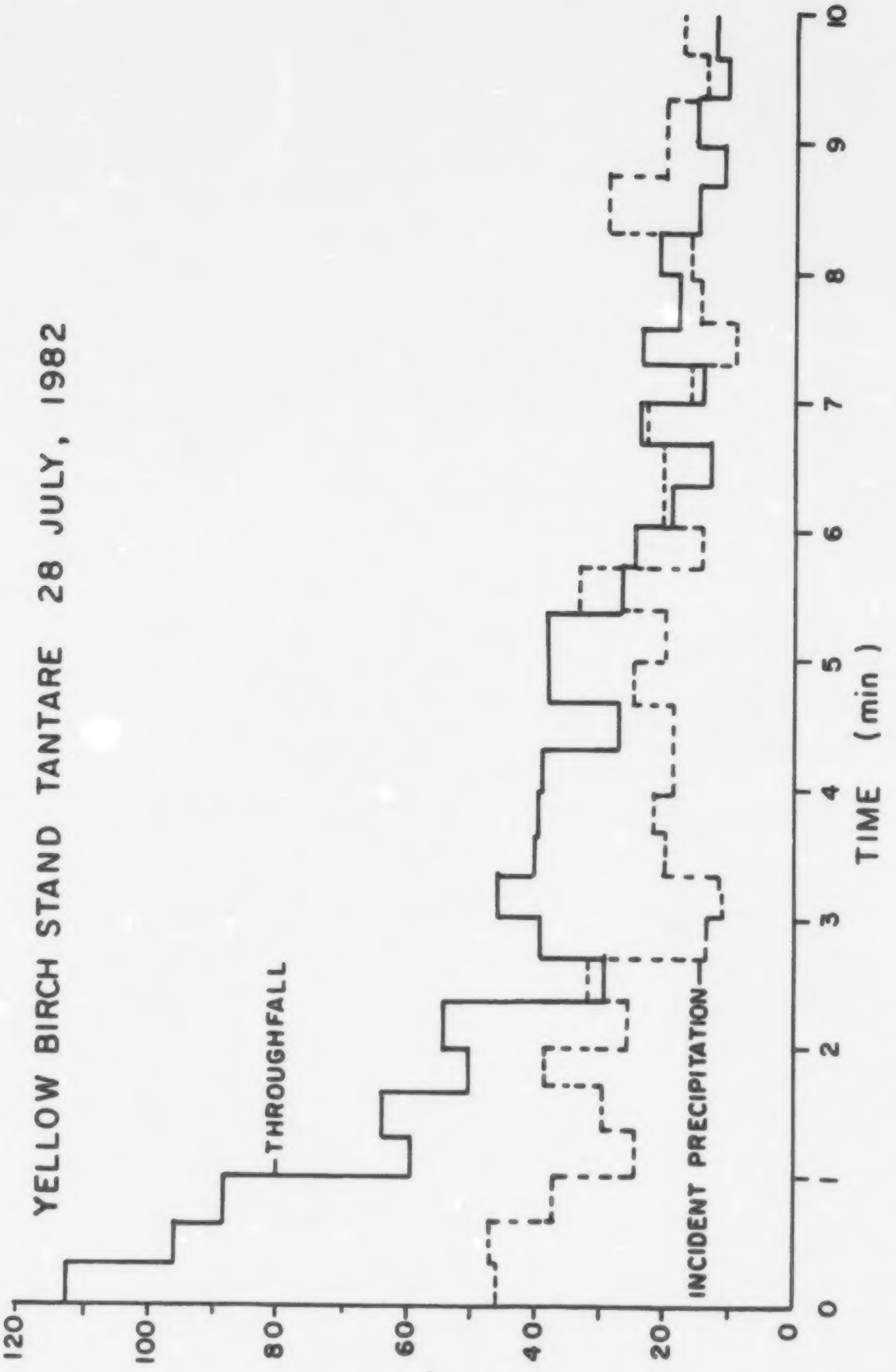

Figure 4. Fe deposition (μg m-2) yellow birch stand, Tantaré, July 28, 1982.

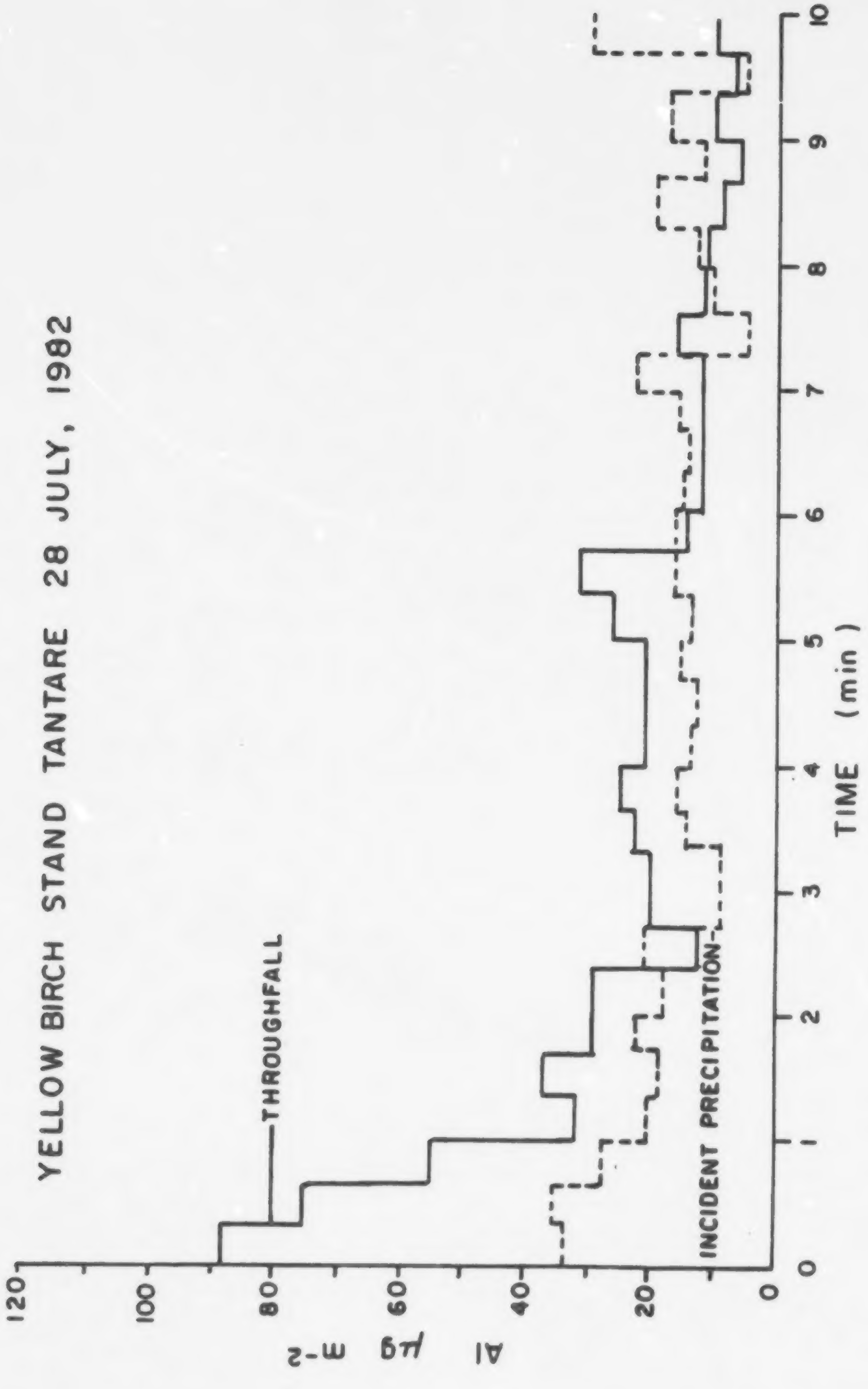

Figure 5. Al deposition (µg m-2) yellow birch stand, Tantaré, July 28, 1982.

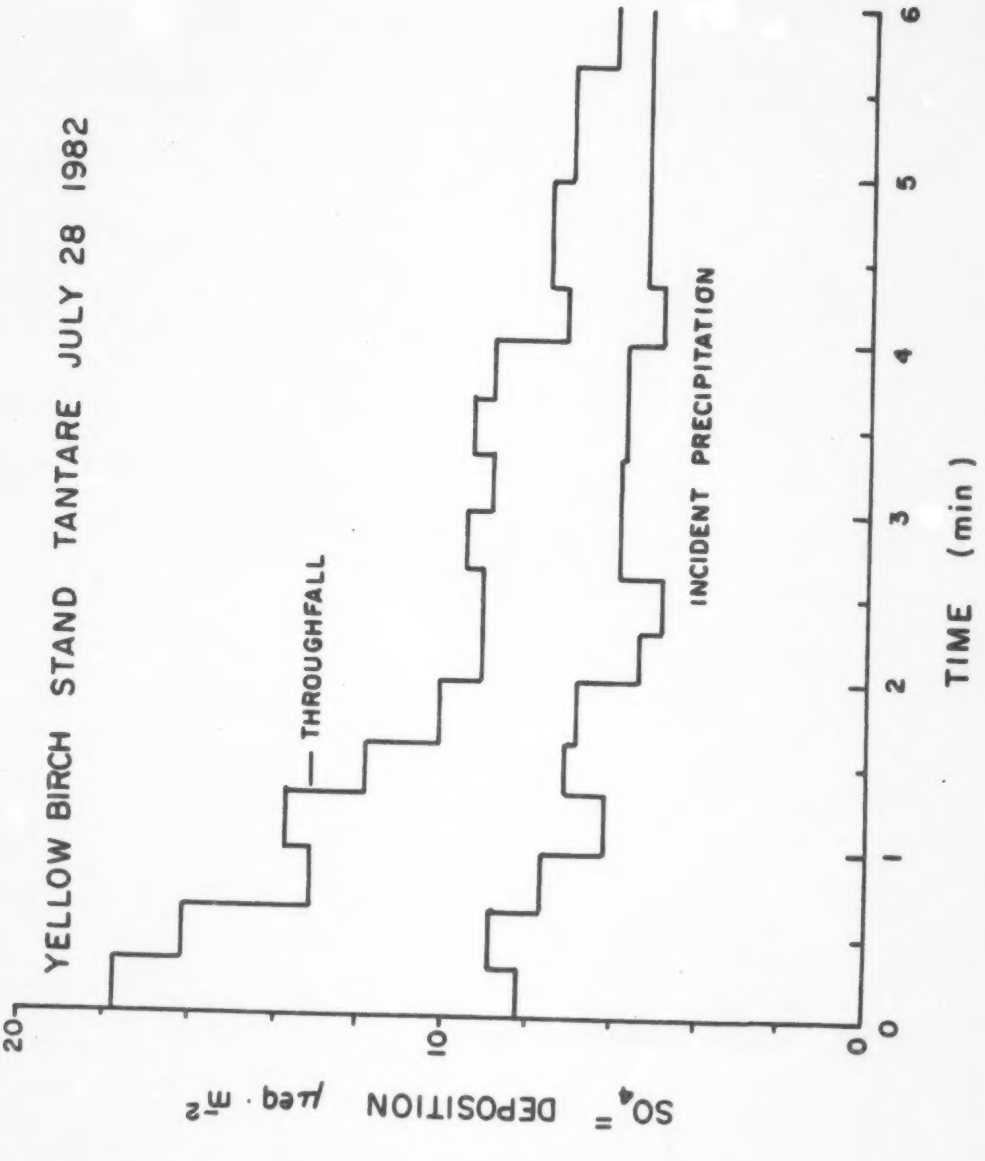

Figure 6. SO_4^{2-} deposition (µeq m^{-2}) yellow birch stand, Tantaré, July 28, 1982.

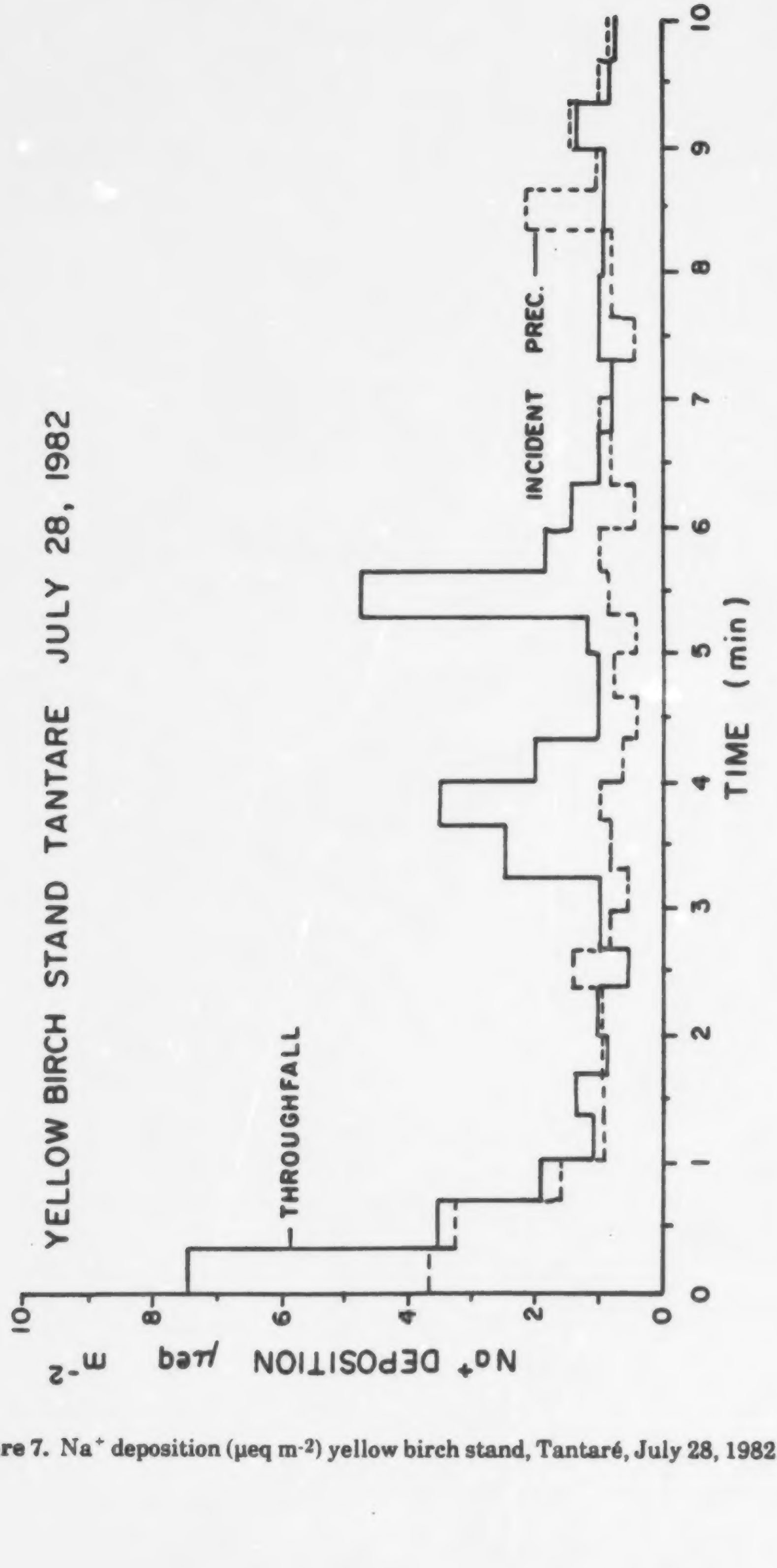

Figure 7. Na$^+$ deposition (μeq m^{-2}) yellow birch stand, Tantaré, July 28, 1982.

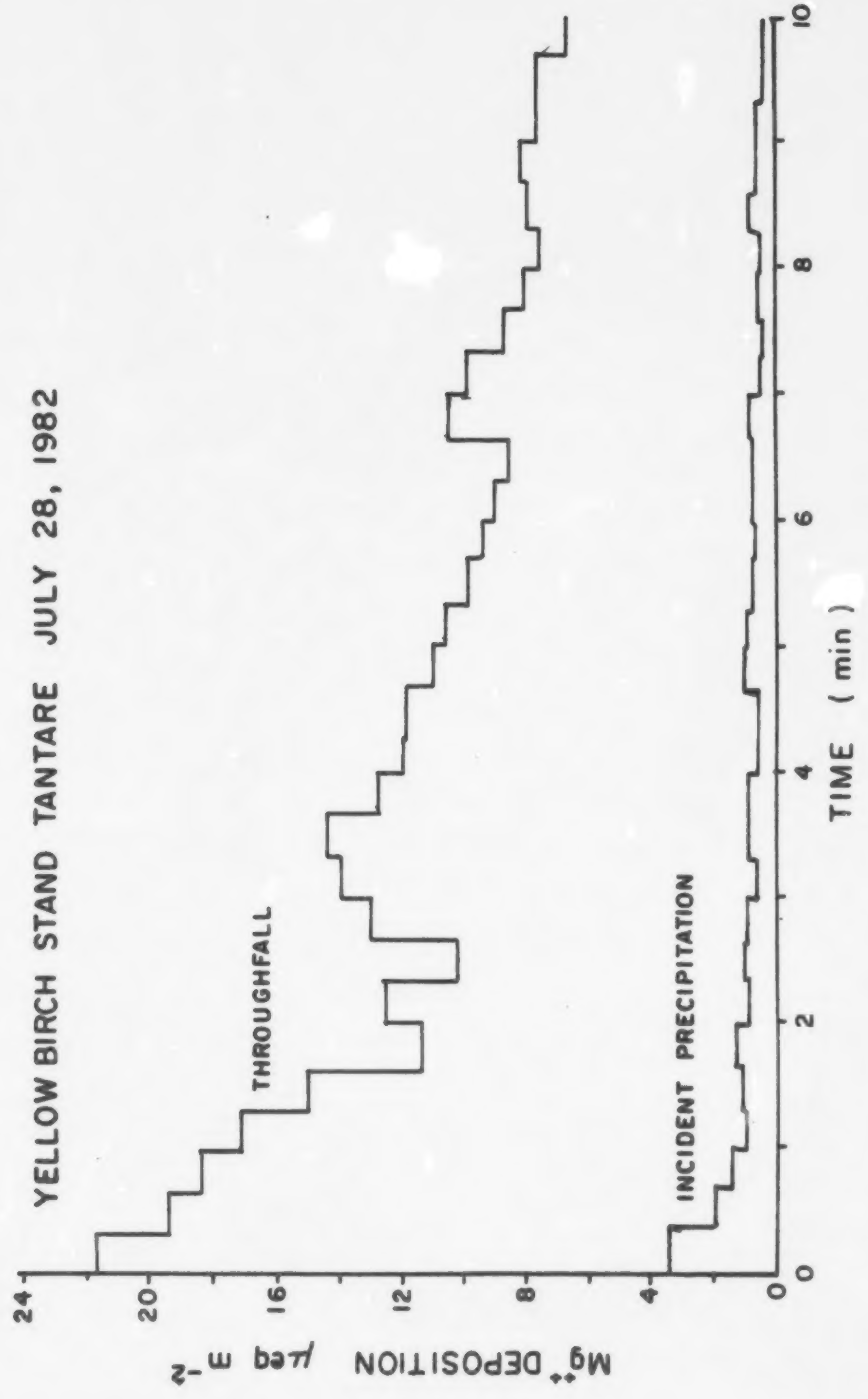

Figure 8. Mg^{2+} deposition (μeq m^{-2}) yellow birch stand, Tantaré, July 28, 1982.

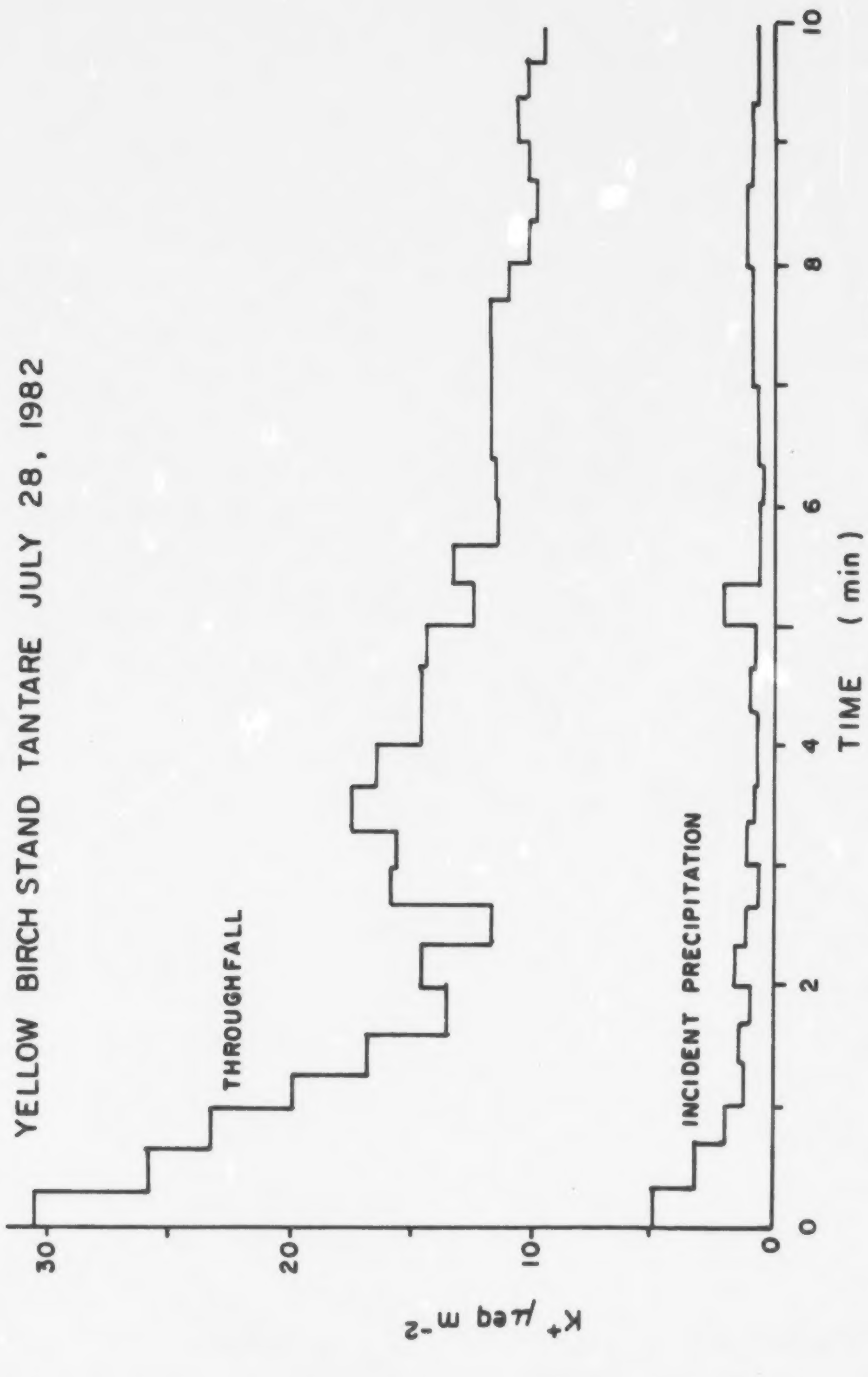

Figure 9. K$^+$ deposition (μeq m^{-2}) yellow birch stand, Tantaré, July 28, 1982.

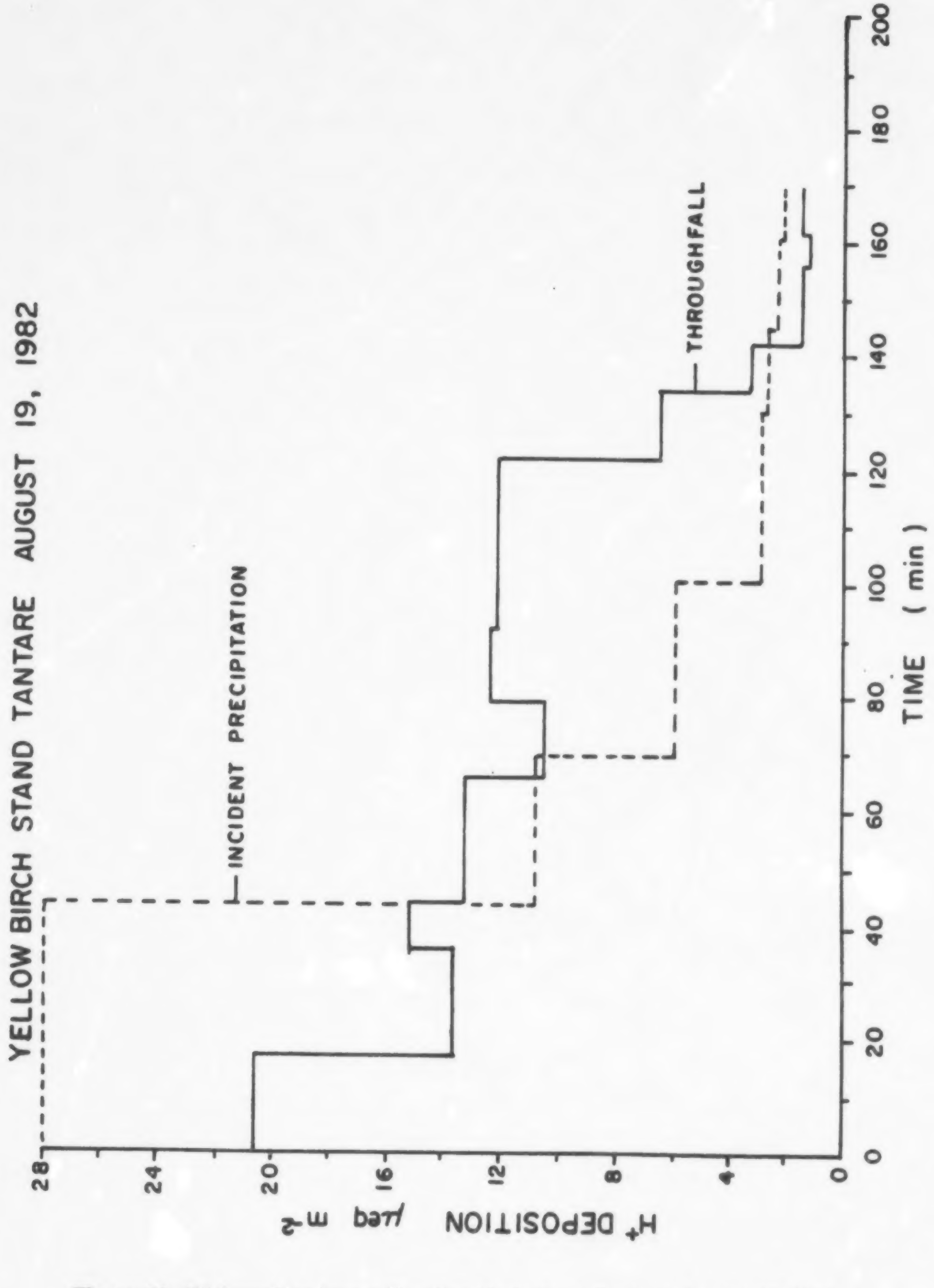

Figure 10. H$^+$ deposition (μeq m^{-2}) yellow birch stand, Tantaré, August 19, 1982.

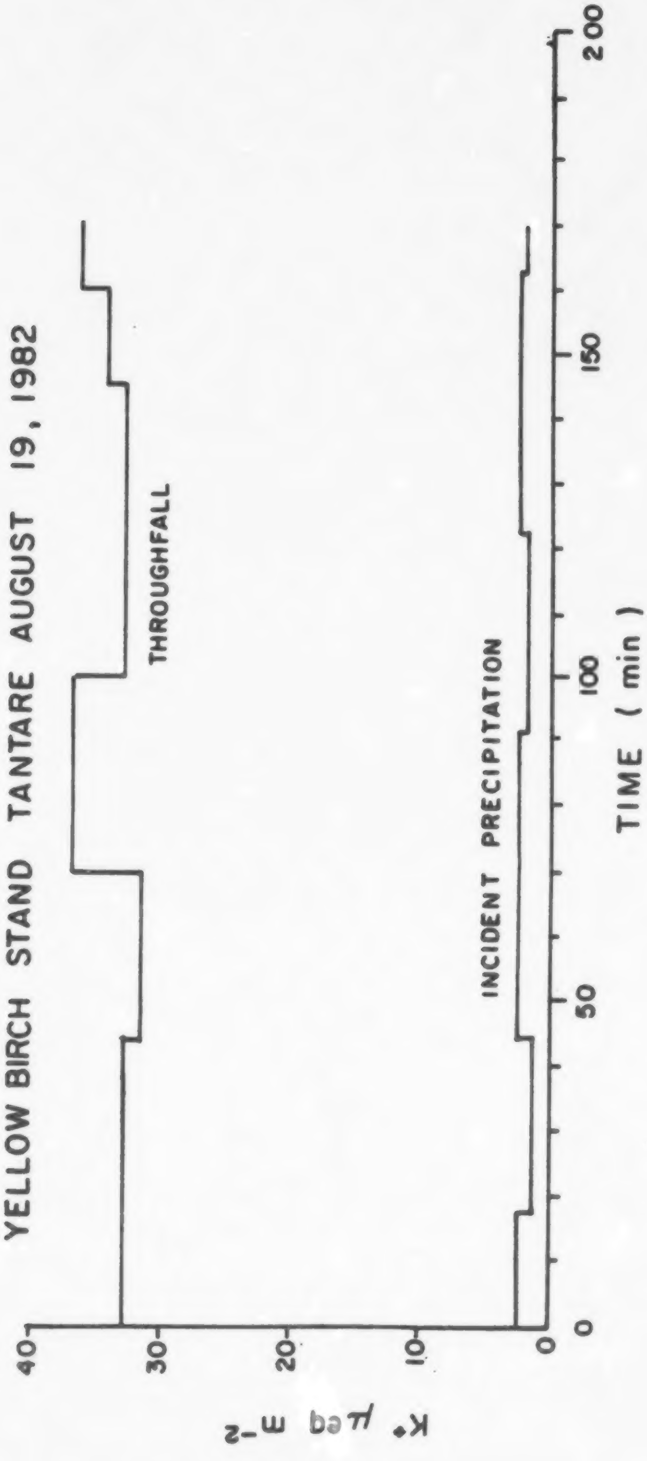

Figure 11. K$^+$ deposition (µeq m^{-2}) yellow birch stand, Tantaré, August 19, 1982.

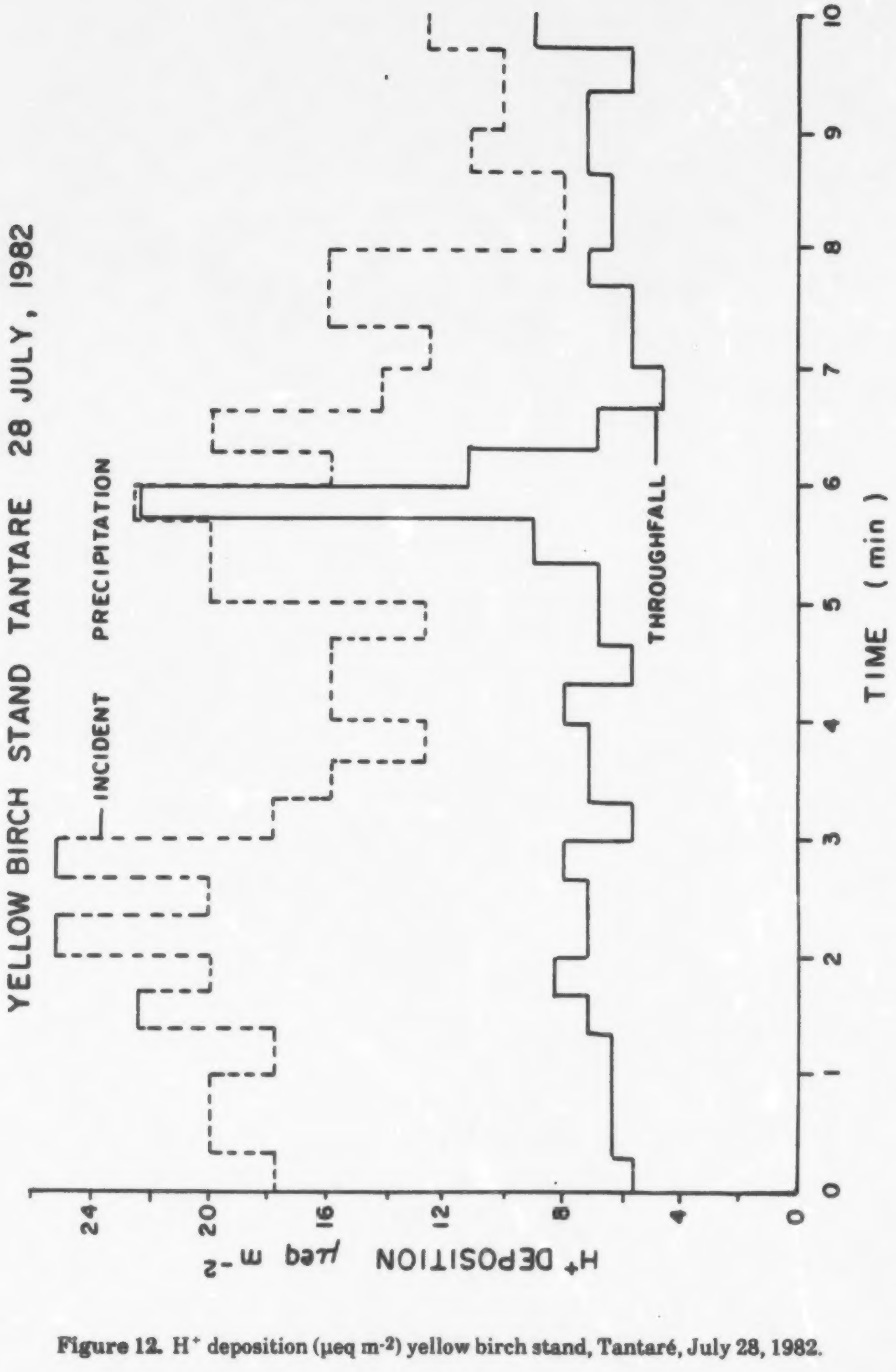

Figure 12. H$^+$ deposition (μeq m^{-2}) yellow birch stand, Tantaré, July 28, 1982.

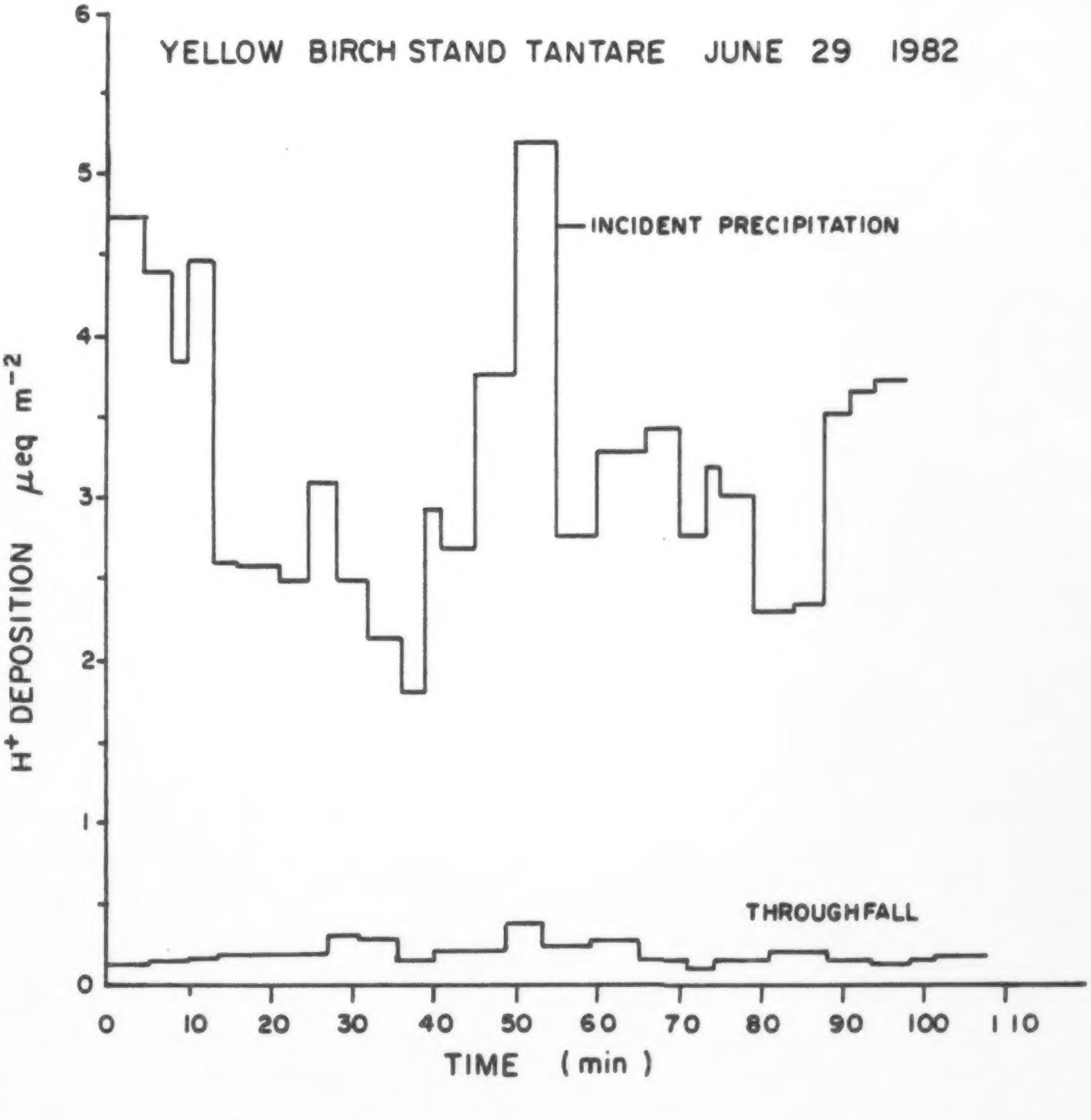

Figure 13. H$^+$ deposition (μeq m^{-2}) yellow birch stand, Tantaré, June 29, 1982.

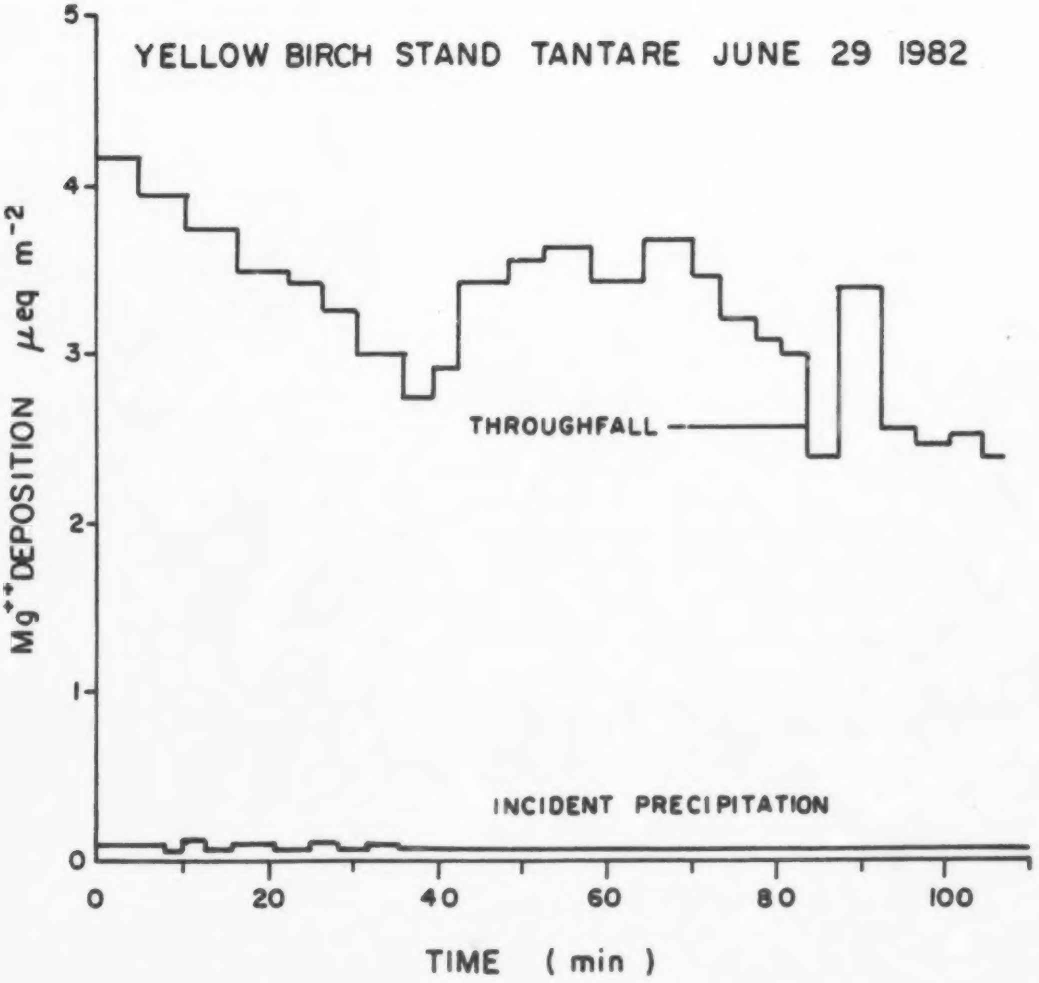

Figure 14. Mg^{2+} deposition (μeq m^{-2}) yellow birch stand, Tantaré, June 29, 1982.

One can observe from the deposition rates recorded during initial sequential samples in Figures 4, 5, 6 and 7 the phenomena of atmospheric rain-out and washout of atmospheric aerosols and dust (Kins 1982) analogous to that of the displaced aerosols on the tree canopy.

All elements with high deposition ratios (Ca^{2+}, Mg^{2+}, Fig. 8; K^+, Fig. 9; Mn) showed similar behavior to that of Fe, Al SO_4^{2-} and Na^+ except that the asymptotic values of the deposition rate obtained after 6 min were very much greater in the case of the throughfall sequential samples than those of the incident precipitation. If we assume that solubilisation or detachment rates of Ca^{2+}, Mg^{2+}, K^+ and Mn deposited aerosols from the canopy are similar to those of Fe, Al, Na^+ and SO_4^{2-} then these asymptotic values should represent the true rates of ion deposition by leaching from the canopy. Leaching rates calculated by this method gave the following values for the event of July 28: Ca^{2+}, 14 μeq mm^{-1} m^{-2}; Mg^{2+}, 16 μeq mm^{-1} m^{-2}; Mn 45 μg mm^{-1} m^{-2}; K^+, 22 μeq mm^{-1} m^{-2}. That this phenomenon of leaching from the canopy proceeds generally irrespective of the acidity of the incoming precipitation can be ascertained from the fact that even when incident precipitation and canopy throughfall attain similar low values for the rates of H^+ deposition (e.g. August 19, Fig. 10) leaching still occurs (K^+, Fig. 11). However, whether these leaching rates are influenced by the H^+ loading of the incident precipitation is difficult to determine. A comparison of sequential Mg^{2+} deposition rates for the July 28 event (Fig. 8) with that of the sequential H^+ deposition rates for the same event (Fig. 12) shows that increases in the H^+ deposition rates of the incident precipitation on the canopy at 2-3 min and 5-7 min after the start of the event are followed closely by similar increases in the Mg^{2+} deposition rate at 3-4 min and ≃7 min. This relationship between Mg^{2+} and H^+ deposition rates may also be seen in the sequential deposition rates of these elements during the June 29 event when a substantial increase of the deposition rate at 40-50 min (Fig. 13) was followed closely by an increase in the Mg^{2+} deposition rate (Fig. 14). Although Mn shows similar behavior to Mg^{2+} during these two events, K^+ does not; at the present time, these leaching deposition rates of ions cannot be related to the H^+ loading in incident precipitation.

Streamwater Quality

Although the influence of the canopy on the incident rainfall results in ground level precipitation inputs of varying H^+ ion concentrations, streamwater mean acidity remains high (H^+, 25.1 μeq L^{-1}) and varies little throughout both the spring-fall season and during individual storms. This is also true for the streamwater concentrations of major ions and most metals. Aluminum concentrations in the stream (Fig. 15) are, however, relatively high (≃ 300-350 μg L^{-1}) and are a prominent characteristic of the acidic waters of the Lake Tantaré system (Ouellet and Jones 1983). Lee and Weber (1982) have invoked the "mobile anion" or "anion leaching" theory to account for the acidification of surface waters rather than acid precipitation *per se*. However, Krug and Frink (1983) have reported that this theory is unsound; at the present time, the exact nature of the control that the soil cover exerts in the acidification of watersheds is unknown. Ulrich (private communication) has related the acidification of surface waters in this region of Quebec not only to increased acid deposition itself but also to the effect it produces on further proton production by biomass utilization. Whatever the importance, or relative importance, of these phenomena, it seems from the quality of the streamwaters that acidification of the Lake Tantaré system is under way; this is also indicated by the sediment profiles reported by Ouellet and Jones (1982) and Ouellet et al. (1984).

CONCLUSION

Interaction between incident precipitation and the vegetative canopy of the yellow birch stand results in the net exchange of major ions and metals of which the deposition ratios increased in the order of $< Pb < H^+ < Al < Na^+ < SO_4^{2-} < Fe < NO_3^- < Ca^{2+} < Mg^{2+} < Mn < K^+$. Elements with ion deposition ratios could, by sequential sampling of certain events, e.g. July 29, be used to estimate the rate of dry deposition washoff and consequently allow the determination of the leaching rates of elements with high deposition values from the canopy. Although individual throughfalls showed substantial variation in chemical quality at ground level this appeared to have no apparent effect on the streamwater quality which remained relatively constant throughout the study period. This suggests that soil and subsoil processes related to soil-water ionic exchange during the movement of water through the drainage basin are the dominant factors in the control of surface water quality as opposed to the acidity of the incident precipitation *per se*.

ACKNOWLEDGMENTS

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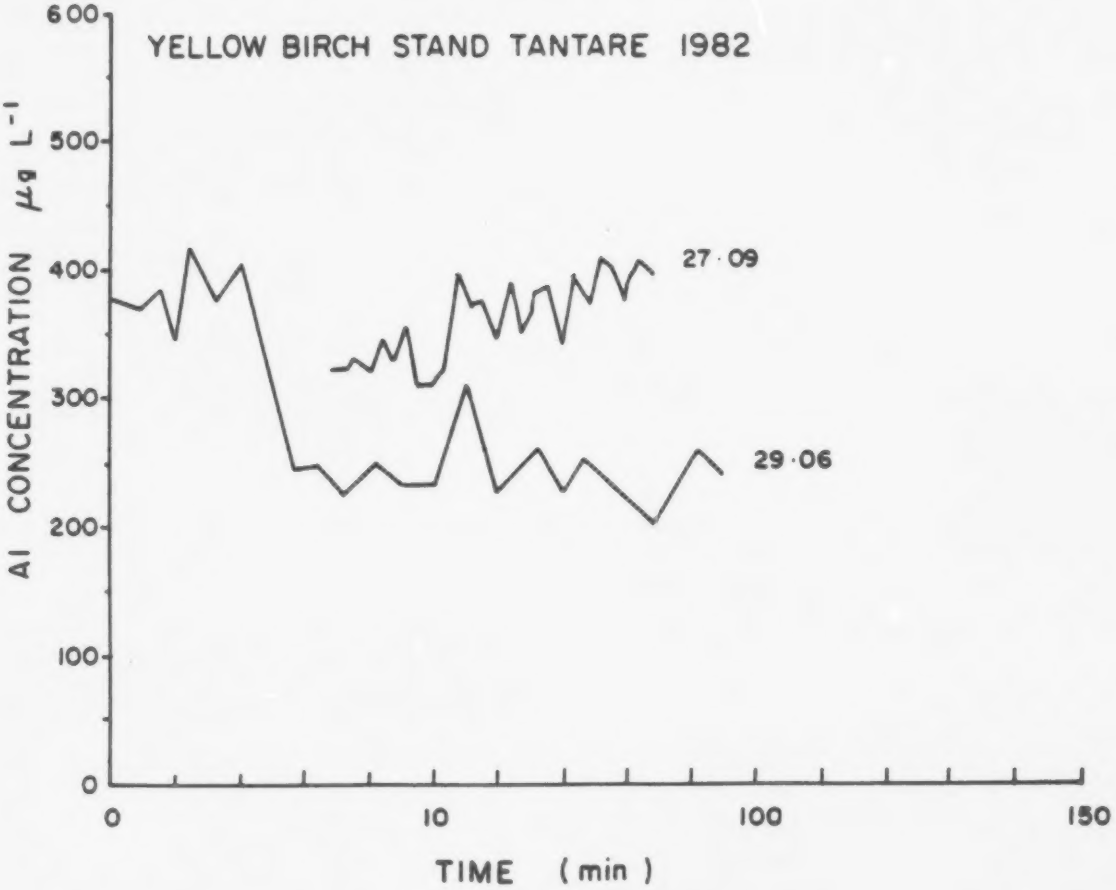

Figure 15. Al concentration (μg L^{-1}) in streamwater, yellow birch stand, Tantaré, 1982.

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Seasonal Precipitation Chemical Characteristics and Their Influence on Stream and Lake Waters in the Laurentides Park Region of Quebec, Eastern Canada

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ABSTRACT

Chemical studies of sequential precipitation (rain) episodes, throughfall, stream and lake waters in a mature yellow-birch forested watershed (Lake Tantaré, Laurentides Park region, Québec) showed that the effect of the canopy on precipitations caused the resultant throughfall to possess greater variability in composition than that observed between individual rain events. Marked differences between throughfall chemical characteristics (e.g.: pH) were, however, not reflected by the major headwater streams (pH 4.4-4.8) draining the watershed, suggesting that the quality of subsurface drainage is more dependent on the total anionic composition of the incoming precipitation and throughfall than on pH considerations alone. Differences in the temporal progression of major cations, anions and heavy metal in the precipitation and throughfall during individual rain events may be attributed to the intrinsic quality of the precipitation, dry deposition wash-off and active tree canopy transport of certain elements. The major area of interest is concerned with the different behavior of chemically similar elements (e.g.: Ca, Mg; Fe, Mn; and Na, K) and organically bound elements (e.g.: P, S). Al present in only low concentrations in both precipitation and run-off is, however, a characteristic of stream and lake waters. Recent increased deposition rates of this element in the lake sediments attest to the progressive acidification of the surface waters in this watershed.

Growth and Nutritional Responses of Yellow Birch Seedlings on Component Mineral Soil Horizons to Acid "Rainwater" Solutions

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ABSTRACT

In a preliminary experiment, inhibitory effects of acid rain simulants on the growth of yellow birch (*Betula alleghaniensis* Britt.) seedlings were largely a consequence of direct foliar damage at pHs below those commonly occurring in ambient rain events in northeastern North America.

To assess the short-term soil-mediated effects of acid rain on plant growth and nutrition, acid "rainwater" solutions were applied to simulated mineral and mixed humus-mineral soil seedbeds sown with yellow birch, avoiding direct contact with seedling foliage. After sowing, ten pots each of Ah, mixed Ah/Bf, Bf and KH_2PO_4-amended Bf (Bf+P) horizon material of a humo-ferric podzol were treated with "rainwater" solutions at a rate of 2.25 cm wk^{-1} for 90 days under greenhouse conditions. "Rainwater" containing background ions was acidified to pH 2.5, 3.0, 3.5, 4.0 and 5.6 with H_2SO_4 and HNO_3 at a 2:1 SO_4^{2-}:NO_3^- ratio (equivalent basis). Seedling foliage was analyzed for total N, S, Ca, Mg, K, P, Mn, Al and Fe. Root Al, Fe and Mn concentrations were also determined. Soils were analyzed for pH, KCl-extractable NO_3^--N and NH_4^+-N, exchangeable Ca, Mg, K, Fe, available P and $CaCl_2$ -soluble Mn and Al.

Accelerated inputs of NO_3^- associated with increasing "rainwater" acidity raised soil NO_3^- -N levels in the Ah, Ah/Bf and Bf substrates under the pH 2.5 treatment. Concentrations of NH_4^+-N in the Ah and Ah/Bf substrates also increased with "rainwater" acidity, possibly an effect of reduced populations of nitrifying bacteria caused by soil acidification. By comparison, inorganic N levels in the Bf+P substrate were very low and showed no treatment, related changes, presumably due to complete seedling utilization of NO_3^--N inputs. The greater amounts of NO_3^- and SO_4^{2-} supplied with increasing "rainwater" acidity increased the uptake of N and S in the foliage and stimulated seedling growth on all substrates (Bf+P > Ah > Ah/Bf) except the Bf, which was severely deficient in P. However, in contrast to S and other elements determined, N (and to a lesser extent P) concentrations in foliage were significantly and inversely correlated with seedling growth on the Ah substrate, indicating a primary N deficiency. Concentrations of N were much lower in seedlings on the Bf+P substrate and accompanied by pronounced deficiency symptoms (i.e. chlorotic leaves).

Acid "rainwater" treatments had no marked effect on the content and concentrations of Ca, K, P and Fe in seedlings grown on the Ah and Ah/Bf substrates. While the content of Mg in leaves was not affected on the Ah substrate, foliar concentrations of Mg decreased significantly with increasing "rainwater" acidity, reflecting a corresponding decline in Mg^{2+} levels on the soil exchange complex. At pH 2.5, foliar concentrations of Mn in seedlings on the Ah substrate increased threefold to toxic levels due to increased solubilization of soil Mn, although toxicity was masked by the stronger NO_3 fertilization effect. Smaller increases in root Al concentrations of seedlings grown on the Bf+P and Ah/Bf substrates also reflected increased solubilization of Al with decreasing "rainwater" pH. However, phosphorus (KH_2PO_4) enrichment of "rainwater" applied to the Bf substrate reduced soil acidification and the availability of Al and Fe overall and from increasing treatment acidity. The results of this study suggest that in the short term N and possibly S inputs from acid precipitation will have a positive effect on tree growth where these nutrients are limiting.

Resistance of the Caribou Lichen (*Cladina stellaris* (Opiz.) Brodo) to Growth Reduction by Simulated Acid Rain

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ABSTRACT

Natural mats of *C. stellaris* growing in the subarctic lichen woodlands of northern Québec were treated in a randomized complete block design with solutions of simulated rain at pH 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 5.6. These solutions were acidified by addition of mixtures of sulfuric and nitric acids to give both 2:1 and 6:1 microequivalent ratios of SO_4^{2-}:NO_3^-. Treatments were applied weekly during the snow-free season. Measurements of the mean annual growth rate before and after two years of treatment were used to assess the potential effects of acid precipitation on net production of this important caribou forage lichen. Analysis of covariance showed no significant effect of either pH or SO_4^{2-}:NO_3^- ratio on the growth of *C. stellaris*. This circum-boreal and very abundant lichen appears to be resistant to at least short-term exposures to acid precipitation.

INTRODUCTION

The metabolic activity of lichens can sometimes, but not always, be altered when the lichen is wetted by acid rather than normal precipitation. Lechowicz (1982) showed that the photosynthetic activity of *Cladina stellaris*, a lichen especially important as winter forage for caribou, was reduced after wetting by even moderately acidic solutions. At pH 4.0 photosynthetic capacity was lowered 27% from normal levels and the lichen took 14% longer to recover from dormancy after being wetted. Similarly, Bailey and Larson (1982) found that the net photosynthetic rate of *Umbilicaria mammulata* collected in February, when stored reserves are at their lowest in northern lichens (Holopainen 1982), was typically as much as 50% lower when wetted by solutions of pH 2.0 compared to pH 6.0; intermediate levels of depression of net photosynthesis were also apparent after wetting at pH 4.0. In contrast, Bailey and Larson (1982) found that neither the net photosynthesis nor respiratory responses of this *Umbilicaria* were affected by the pH of the wetting solutions for samples collected in August when lichen reserves are highest (Holopainen 1982). Lane and Puckett (1979) showed that for both *Cladina rangiferina* and *Lobaria pulmonaria* the activity of phosphatase, an enzyme involved in lichen mineral nutrition, actually increased as pH dropped from 8.9 to 2.2. Given the dominant role of gas exchange rather than mineral nutrition in determining rates of lichen growth (Lechowicz 1981), it is still most reasonable to expect that the action of acid precipitation in some seasons can reduce the net annual productivity of lichens (Lechowicz 1982; Gilbert 1980). To test this supposition a series of simulated acid rain plots were established in a subarctic lichen woodland to monitor the effects of chronic acid precipitation on the growth of *Cladina stellaris*, a lichen which is a dominant component of many boreal and subarctic ecosystems throughout the northern hemisphere (Ahti 1977).

STUDY AREA

The acidification trials were conducted in a previously undisturbed lichen woodland near Schefferville, Québec at about 54°48'N, 66°55'W and at an altitude of about 540 m. The subarctic site represents a fully mature lichen woodland community typified by an open, almost park-like aspect (Figure 1) and a relatively species-poor plant cover (Table 1). The trees, mostly black spruce (*Picea mariana*), with some white spruce (*P. glauca*) and larch (*Larix laricina*), are widely spaced. Judging from increment-core data, the largest trees are in excess of 125 years old (Lechowicz, unpublished data; Lucarotti 1981). The sparse shrub layer is predominantly dwarf birch (*Betula glandulosa*), blueberry (*Vaccinium angustifolium*), and Labrador tea (*Ledum groenlandicum*). An 8-cm-thick mat of the caribou lichen, *Cladina stellaris*, carpets 73% of the ground surface. Similar lichen woodlands are common both around Schefferville (Rencz and Auclair 1978) and throughout the Canadian boreal and subarctic regions (Kershaw 1977; Ahti 1977; Carroll and Bliss 1982; Clayden and Bouchard 1983).

EXPERIMENTAL DESIGN AND PROCEDURES

The basic experiment consisted of weekly waterings of the *Cladina stellaris* mat in this lichen woodland community with artificial rain solutions ranging from pH 2.5 through pH 5.6. The composition of the artificial rain solution following Shriner (1978, Table 11-7) was 0.22 mg L^{-1} calcium, 0.06 mg L^{-1} magnesium, 0.12 mg L^{-1} sodium, 0.08 mg L^{-1} potassium, 0.22 mg L^{-1} ammonium, 0.53 mg L^{-1} sulfate, 0.74 mg L^{-1} nitrate, 0.42 mg L^{-1} chlorine, 0.002 mg L^{-1} hydrogen, and 0.13 mg L^{-1} bicarbonate. The rain solution was acidified with either 2:1 or 6:1 microequivalent ratios of sulfate:nitrate. These two acidification ratios were chosen to reflect the range of strong acid compositions most likely for precipitation in eastern North America (US/Canada Work Group 1981; Kerekes 1980; Raynal et al. 1980; Fisher et al. 1968). The two ratios also provide data on the possibility that any negative effects of acidification may be countered by nitrogen enrichment of the lichen. The watering treatments began in summer 1981. At each watering the equivalent of 2 mm of rain was applied to each plot as a fine mist; this is just sufficient to saturate the lichen mat. Care was taken to prevent wind drift between adjacent plots during watering. In 1981 nine waterings were applied from July through September, and in 1982 10 waterings from June through August. In this paper the mean annual growth rates of *Cladina stellaris* are compared after these two summers of treatments using samples collected in September 1982.

The treatments were applied in a randomized complete block design (Cochrane and Cox 1957) involving 16 treatment plots in each of five blocks. The individual treatment plots are 1 m x 1 m with 0.5-m buffer strips between them and at the periphery of the block. Each block of 16 plots is a 6.5 m x 6.5 m square, sited between the trees in the lichen woodland. Twelve of the treatments in each block are: watering with artificial rain solutions acidified with either 2:1 or 6:1 ratios of sulfate:nitrate to pH 2.5, 3.0, 3.5, 4.0, 4.5 or 5.0. In addition, two unwatered plots were used as controls and two others were watered just with artificial rain of pH 5.6. Figure 1 illustrates a block of 16 treatment plots at the experimental site.

The mean annual growth rate of lichens like *Cladina stellaris* can be readily monitored since only one whorl of branches is produced each year (Andreev 1954; Lechowicz, personal observation). An individual branch whorl continues to grow for about nine years after its inception (Lechowicz 1983). In this study, the mean annual biomass increment based on the youngest six branch whorls was used to compare lichen response to the acidification treatments. Lechowicz (1983) has shown in *Cladina stellaris* that although the youngest six branch whorls comprise only 18% of the living thallus biomass, they account for 50% of potential photosynthetic activity. These metabolically active tissues should serve as especially sensitive indicators of any effects of acid precipitation on growth. The dry biomass of one six-year growing tip was measured in each lichen sample using a Cahn model G2 electrobalance accurate to 0.01 mg; four samples were taken in each treatment plot. Growth increments are expressed as an average over the six-year period in mg (dry biomass)/yr^{-1}.

In a natural lichen woodland, it is impossible to assure that all plots have the same growth rates prior to treatment. Fortunately, analysis of covariance can be used statistically to correct for any pretreatment differences that would confound the analysis of responses to the acidification treatments (Huitema 1980). This analysis essentially compares the growth responses to the diverse treatments after adjustment for any growth differences among plots before the experimental waterings were

Figure 1. Aspect of an experimental block located between the widely spaced trees at our study site near Schefferville, Québec.

Table 1. Phytosociology of the research site

Trees	Stems/ha	Mean dbh, cm	cm dbh/ha	no. saplings/ha
Picea mariana	380	14.0	5330	350
Picea glauca	30	13.8	414	70
Larix laricina	50	13.0	650	60

Shrubs and ground cover		
Vascular Plants:	*Betula glandulosa*	23.3%
	Vaccinium angustifolium	14.0%
	Ledum groenlandicum	10.3%
	Empetrum nigrum	1.8%
	Lycopodium annotinum	0.8%
	Vaccinium uliginosum	0.7%
	Vaccinium vitis-idaea	0.6%
	Festuca ovina	0.6%
	Kalmia polifolia	0.2%
Cryptogams:	*Cladina stellaris*	72.8%
	Stereocaulon paschale	6.0%
	Cladina mitis	5.6%
	Cetraria islandica	0.6%
	Dicranum fuscescens	0.3%
	Cladina rangiferina	0.2%
	Cladonia deformis	0.2%
	Cladonia gracilis	0.1%
	Cladonia ecmocyna	0.1%
	Umbilicaria hypoborea	0.1%
	Nephroma arcticum	0.1%
	Pleurozium schreberi	0.1%
	Cetraria nivalis	0.1%
Bare Ground:		2.1%

begun. Samples collected in June 1981 were measured as described above to determine the pretreatment growth rates used as a covariate in these analyses. All growth data were log-transformed before analysis. Comparisons of particular treatments were made using preplanned contrasts rather than multiple comparison tests (Freund and Littell 1981). All analyses were done using the GLM procedure in the 79.5 release of the Statistical Analysis System (SAS Institute 1982).

RESULTS

There are no significant differences among the overall growth responses of *Cladina stellaris* treated for two summers with simulated acid rain solutions (Figure 2, Table 2). The growth of lichens

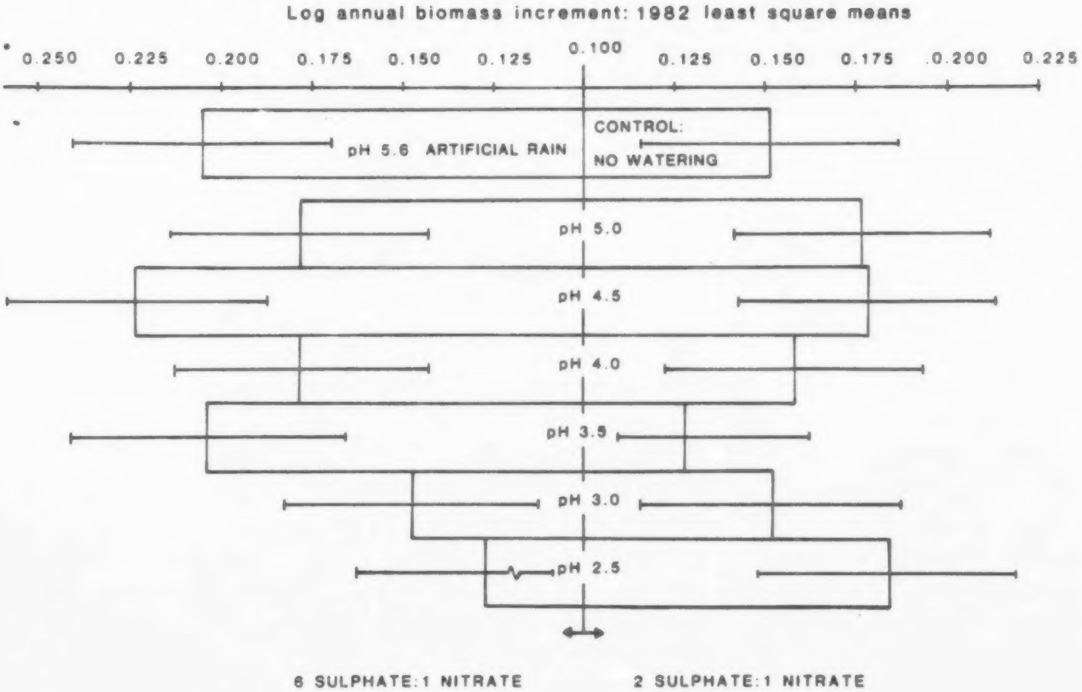

Figure 2. Growth increments for *Cladina stellaris* after two summers under different levels of acidification treatment. The means are adjusted by analysis of covariance to eliminate any pretreatment differences in growth. The figure shows the least square means of five blocked replicates with their standard errors.

Table 2. Analysis of covariance for the 1982 log mean growth increment

Source of variation	df	SS	MS	F	P
Block	4	0.2177	0.0544	8.62	0.0001
Treatment	15	0.0922	0.0061	0.97	0.494
Covariate	1	0.0026	0.0026	0.41	0.524
Error	59	0.3726	0.0063		
Total	79	0.6850			

after acidification with a 2:1 ratio of sulfate:nitrate did not differ significantly from that of lichens watered with artificial rain at pH 5.6. Acidification with a ratio of sulfate:nitrate did lead to changes in growth approaching significance ($p=0.12$), but with no apparent trend on pH (Figure 2). The watering treatment itself resulted in higher growth rates but these were not quite significantly different from the unwatered controls ($p=0.11$); the biomass of the youngest six branch whorls of *Cladina stellaris* watered weekly with artificial rain of pH 5.6 increased an average of 2.8 mg yr^{-1} compared to only 1.8 mg yr^{-1} in unwatered controls. There were no significant differences in growth among lichens watered with 2:1 versus 6:1 microequivalent ratios of sulfate:nitrate ($p=0.43$). There is, however, some indication that growth may be reduced in the pH 2.5 ($p=0.14$) and pH 3.0 ($p=0.09$) treatments compared to the pH 5.6 treatment. By the end of the summer discoloration of the thallus was apparent in these more acid treatment plots.

DISCUSSION

Lichens are unusually sensitive to a variety of environmental pollutants, often in sufficiently low concentrations that they can be used as indicators of chronic pollution levels (Richardson and Nieboer 1981). Air pollutants like sulfur dioxide and fluorine which form acids when absorbed by a wet lichen have especially deleterious effects on lichen growth processes and on lichen survival (Skye 1979; Richardson and Nieboer 1981). It is, therefore, surprising that acidification by nitric and sulfuric acids in simulated rain solutions has not significantly affected the growth of *Cladina stellaris* in subarctic Québec. This widespread and dominant lichen in many northern ecosystems (Ahti 1977) appears to be resistant to at least short-term exposures to even extremely acid precipitation.

The possibility remains, however, that effects on growth are gradual enough to fall below the detection limits set by our experimental methods and design. Although the basic design cannot be altered, the precision of estimated growth responses (Figure 2) could be improved by increasing the number of six-year segments sampled from each plot. This would allow better discrimination of small but significant differences among the treatment plots. The likelihood of discerning any small effects on growth will also increase with continued exposure to acidification, because as treatment continues more of the sampled six-year segment will have been wholly formed under the experimental regime. At present, a portion of the sampled thallus segment grew before treatment. It is also possible that continued acidification will eventually overcome any resistance mechanisms that may be preventing acidification effects on growth after only two summers of treatment. In this case there could be an abrupt reduction of growth after a more extended exposure to acidification. To investigate all these possibilities, the experiment is being continued.

ACKNOWLEDGEMENTS

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Influence of Acidification on Metal Uptake by Plants

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ABSTRACT

Increased mobility of metals as a result of soil acidification may affect their availability to plants. The present work is concerned with the possible influence of soil acidification on plant uptake of aluminum, iron, and manganese, major elements in silicate rocks.

A study of birch in a local acidification gradient indicates a strong influence on metal uptake. For example, the manganese content of *Betula pubescens* increases and the iron content decreases with increasing distance from the source.

In a comparison of coniferous forest ecosystems in southern and central Norway, metal uptake in plants growing in soils with different acid-base conditions is studied. Corresponding ecosystems in the two regions are compared in search of possible effects of the great difference in exposure to acid precipitation that exists between different parts of the country. Certain spruce ecosystems in southern Norway appear to show higher contents of aluminum in soil extracts and in the wood anemone, *Anemone nemorosa*, than corresponding ecosystems in central Norway.

INTRODUCTION

Acidification from natural and anthropogenic processes may bring about a variety of chemical changes in the soil (Malmer 1976). Recently, great interest has been focused on the increased leaching of aluminum in forest soils due to acid precipitation, which may possibly have serious consequences for forestry in central Europe (Ulrich et al. 1980). As the southern part of Scandinavia also receives a significant amount of acidifying substances through the atmosphere, it seems appropriate to watch for possible long-term effects on natural soils and vegetation in this area.

Soil acidification may affect the availability of metals to plants, for example, by increasing the weathering by clay minerals and by leaching metal ions from the cation exchange complex. The ultimate effect on plant uptake probably depends on soil factors such as pH, parent material, clay content, and organic matter content and is, therefore, difficult to estimate in each case. The present work is part of a research program,[1] the main objective of which is to elucidate the extent to which the acidification of natural soils leads to a change in metal uptake in plants and animals in the ecosystems concerned. In the Norwegian part of this program, the subject of the present paper, the problem is approached in three ways:

A. A study of uptake of metals by plants in an acidification gradient arising from a strong local SO_2-source. Birch plants were selected at varying distances from the source and analyzed.

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[1] This research program, initiated and supported by the Nordic Council of Ministers, is carried out in cooperation with Prof. G. Tyler and collaborators, University of Lund, Sweden.

B. A study of metal uptake in plants from coniferous ecosystems in southern and central parts of Norway. Metal uptake in plants growing in soils with different acid-base conditions was studied in each region. Corresponding ecosystems in the two regions were compared to observe possible effects due to the great difference in exposure to acid precipitation in different parts of the country.

C. A comparison of the metal contents of herbarium material from 1870 to 1920 with contemporary material of the same plant species collected from the same localities during the same part of the season, to determine whether the substantial increase in acid precipitation in southernmost Norway in recent decades has had any influence on the metal uptake in plants.

In the present paper, a brief description of the experimental design is given, and some preliminary results are presented. To date, results are available only from the above subprojects A and B; the main emphasis has been on metals that are major elements in silicate rock: aluminum, iron, and manganese.

EXPERIMENTAL

Study Areas

The locations of the study areas selected for the subprojects A and B are shown in Fig. 1.

A. The sampling sites are located in a birch forest on podzolic soil in the area around a copper smelter in northern Norway (Sulitjelma). About 20 000-30 000 tons of SO_2 are emitted from the smelter yearly.
Simultaneous emission of heavy metals (Cu, Zn, Pb, Cd) is an additional complicating phytotoxic factor.

B. Eighty localities representing pine and spruce ecosystems in southern Norway (Aust-Agder and Telemark) and central Norway (Trondelag) were selected. The following vegetational types were represented:
Pine forest with *Calluna vulgaris*
Spruce forest with *Vaccinum myrtillus*
Spruce forest with low ferns
Spruce forest with low herbs and grasses

The forest stands were on either brown earth or podzol soil.

Sampling and Analysis (A and B)

Soil and vegetation samples were collected by the bulking technique, each sample representing an area of about 100 m^2. Soil samples were taken from the humus layer (3-5 cm depth) and from the mineral soil (12-15 cm depth).

Soil samples were analyzed for pH(H_2O), pH(KCl), loss on ignition, plant-available calcium, magnesium, potassium, sodium (extraction with 1M ammonium acetate, pH 7.0), cation exchange capacity, base saturation, and plant-available aluminum, iron, and manganese (1M ammonium acetate, pH 4.8).

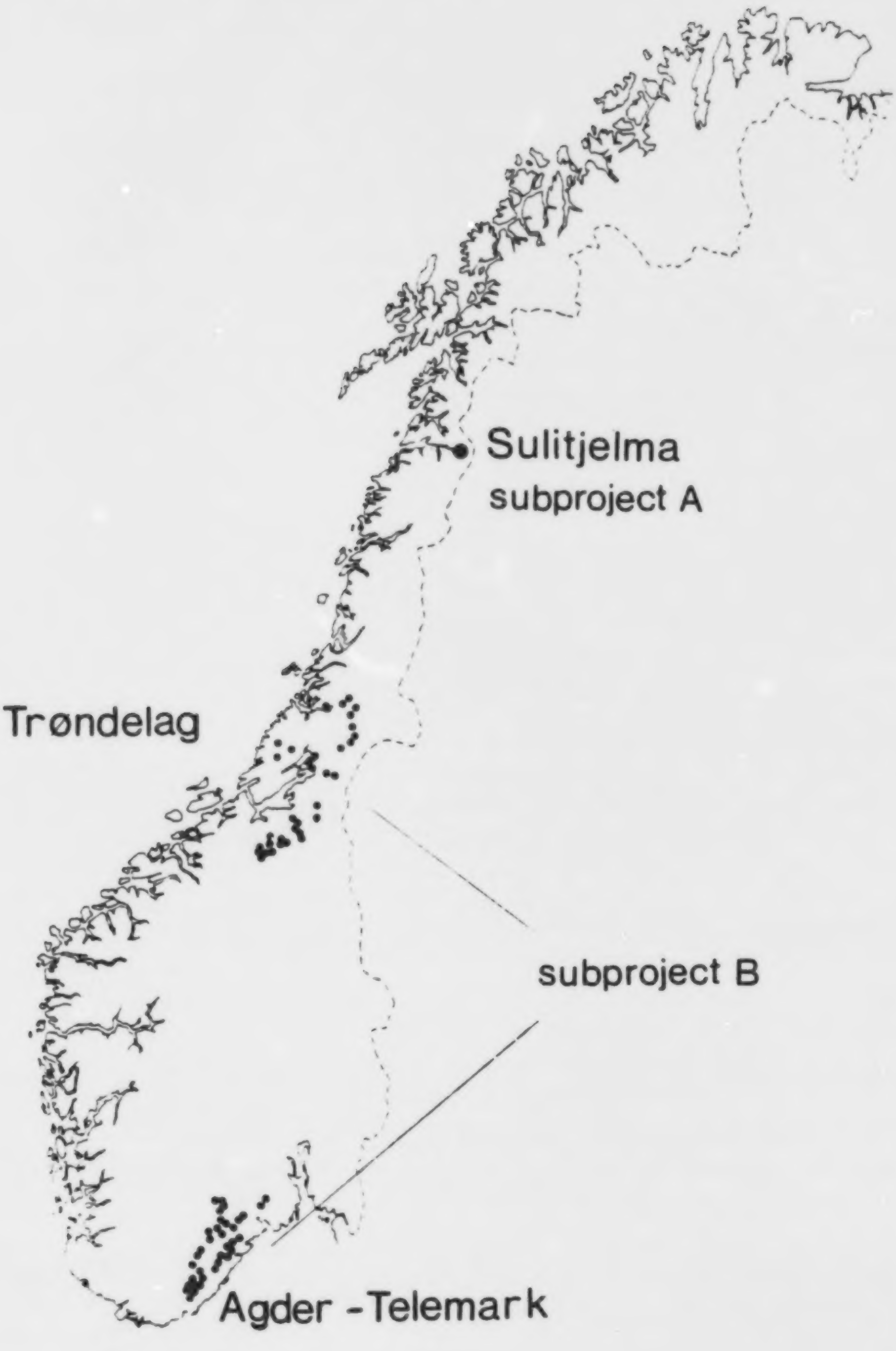
Sulitjelma
subproject A
Trøndelag
subproject B
Agder -Telemark

Figure 1. Map of Norway showing the localities studied in subprojects A and B.

Vegetation samples were analyzed for aluminum, iron, and manganese by atomic absorption spectrophotometry after digestion in concentrated nitric acid.

For project A, vegetation samples and soil extracts (1M ammonium acetate, pH 4.8) were also analyzed for heavy metals (Cu, Zn, Pb, Cd).

RESULTS AND DISCUSSION

Some typical results from subprojects A and B are presented in a preliminary form.

Subproject A

Fig. 2 shows metal contents of *Betula pubescens* twigs found to the west of the Sulitjelma smelter. Content of copper and zinc decreases with increasing distance from the smelter probably as a result of heavy metal deposition. Increasing iron content near the smelter may be caused by increased iron solubility due to higher soil acidity.

In Fig. 3 the manganese content in leaves of three different plant species west of the smelter is shown as a function of distance. In Fig. 4, the plant-available manganese, copper, and zinc, expressed as a percentage of the cation exchange capacity, are plotted. The lower manganese content in plants growing near the smelter could be explained by leaching of Mn(II) from the humus layer due to exchange with hydrogen ions and possibly also with heavy metal cations emitted from the smelter.

Subproject B

Some soil characteristics of the humus layer for different vegetational types in southern and central Norway are shown in Table 1. The soil pH appears to be consistently lower in oligotrophic coniferous forests in southern Norway as compared to corresponding ecosystems in central Norway. The base saturation is significantly lower in spruce forests of southern Norway even in the more eutrophic groups. This indicates that the process of soil acidification has gone further in the region studied in southern Norway than in the corresponding region of central Norway. Although a contribution from acid precipitation to this development cannot be ruled out, it is not possible, at this stage, to estimate the significance of acid precipitation relative to regional differences in soil acidification caused by natural factors.

Fig. 5 shows base saturation versus pH in the humus layer of each individual sample plot. The regional differences in soil acidity depicted in Table 1 are shown even more clearly in this graph. Apparently the residual buffer capacity of soils in some eutrophic spruce forests of southern Norway is quite limited. These forests may not be able to tolerate an accelerated acidification of the soil for a long period of time without considerable ecological consequences.

Plant-available aluminum in surface soils is shown in Table 2 as mean values for the different vegetational types in the two regions. Whereas the levels are similar in the oligotrophic forests, the extractable aluminum is substantially higher in the soils of eutrophic spruce forests in southern Norway, indicating a higher rate of acidification in this area. This result corresponds very well with the evidence expressed in Fig. 5.

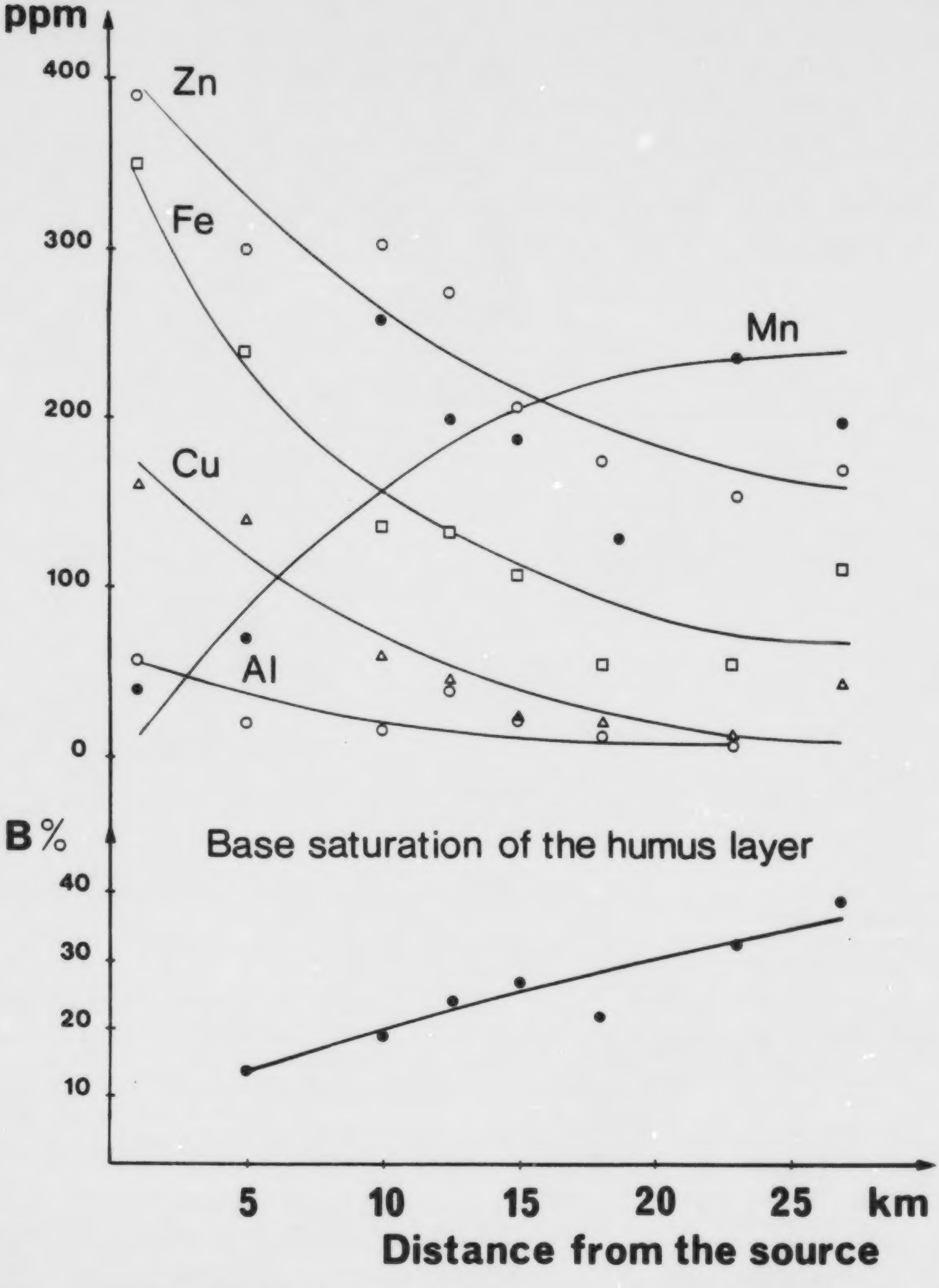

Figure 2. Metal contents in birch (*Betula pubescens*) twigs west of the Sulitjelma smelter.

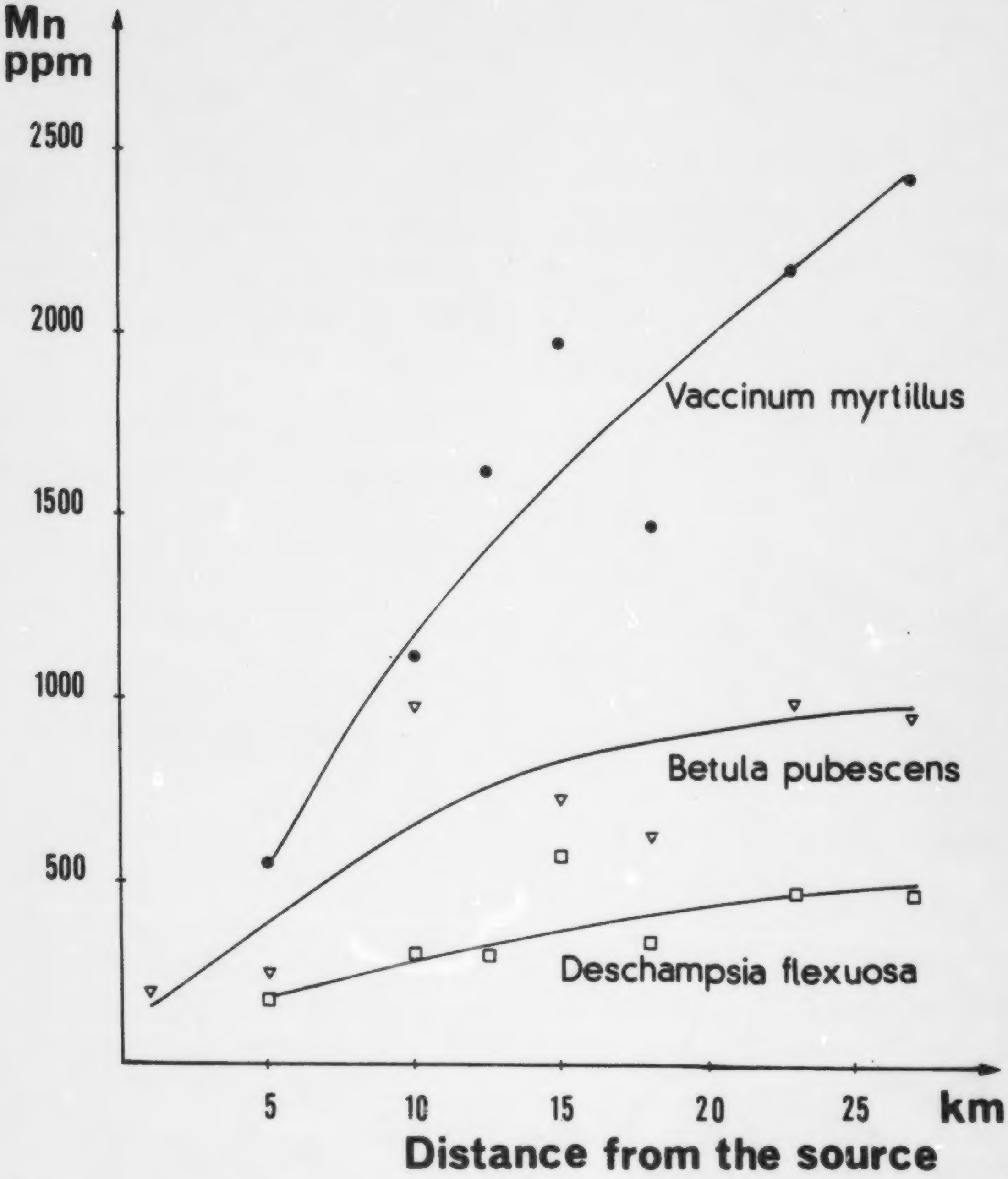

Figure 3. Manganese content in leaves of three different plant species west of the Sulitjelma smelter.

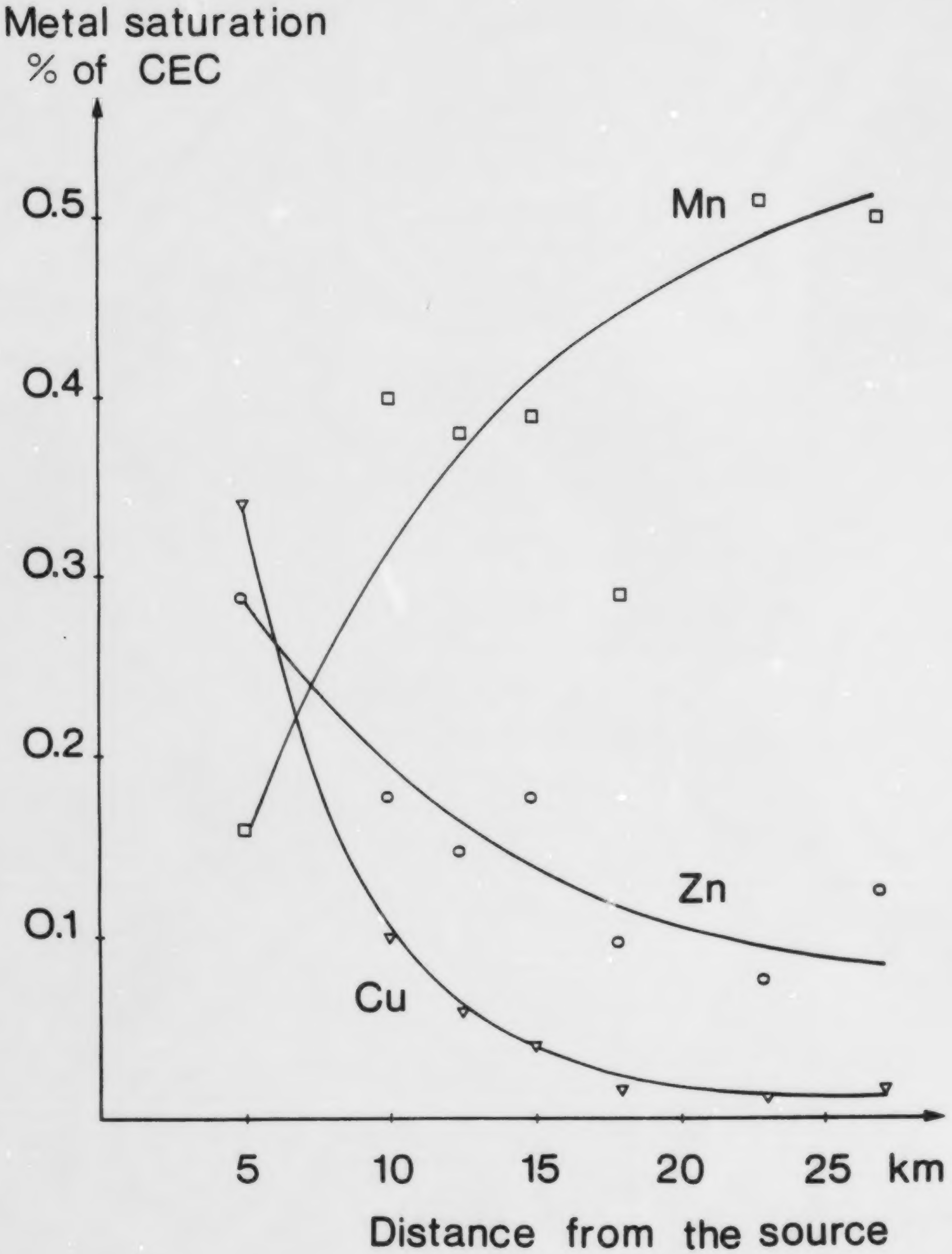

Figure 4. Plant-available content of manganese, copper, and zinc west of the Sulitjelma smelter, expressed as a percentage of the cation exchange capacity of the humus layer.

Table 1. Soil characteristics of the humus layer in different vegetational types. SN: southern Norway; CN: central Norway; P: Podzol; B: Brown earth; PB: Transition type between podzol and brown earth.

Vegetational types	Region	pH (H_2O)	Base saturation (%)	Main soil profile
Pine forest with *Calluna vulgaris*	SN CN	3.74 3.92	18.6 ± 3.6 20.4 ± 8.1	P
Spruce forest with *Vaccinum myrtillus*	SN CN	3.65 3.80	13.5 ± 2.1 20.5 ± 3.3	P
Spruce forest with low ferns	SN CN	3.98 3.93	16.5 ± 6.3 23.3 ± 5.9	P, PB
Spruce forest with low herbs and grasses	SN CN	4.36 4.45	19.1 ± 9.5 35.2 ± 10.5	B, PB

Table 2. Plant-available aluminum in humus samples from coniferous forest ecosystems in southern (SN) and central Norway (CN).

Vegetational types	Extractable aluminum (NH_4OAc, pH 4.8), ppm	
	SN	CN
Pine forest with *Calluna vulgaris*	16.1 ± 4.2	25.9 ± 22.8
Spruce forest with *Vaccinum myrtillus*	18.6 ± 7.0	16.0 ± 9.9
Spruce forest with low ferns	96.1 ± 142.4	23.6 ± 13.0
Spruce forest with low herbs and grasses	147.6 ± 68.6	50.0 ± 29.2

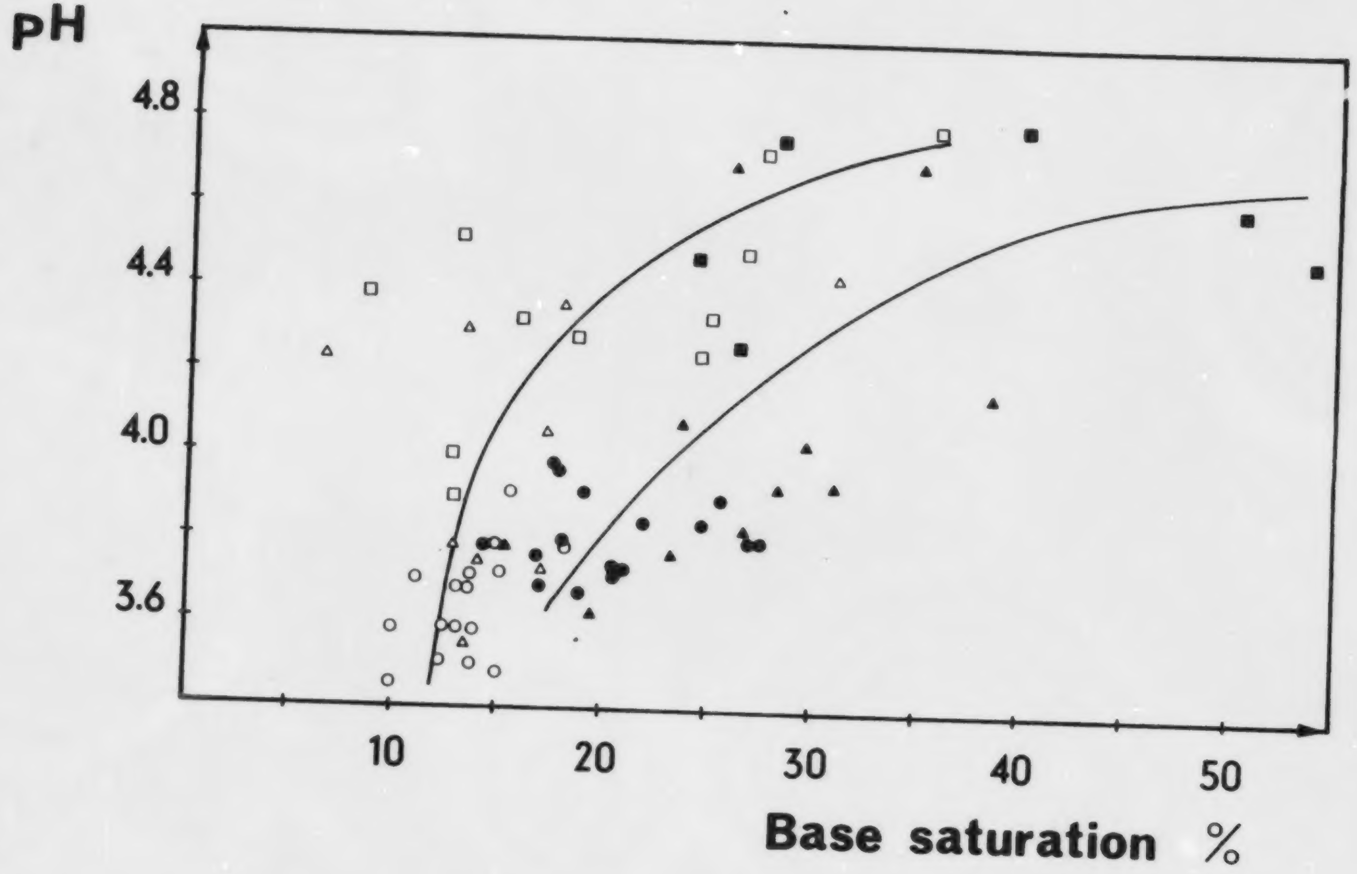

Figure 5. pH(H_2O) versus base saturation for humus samples from spruce forests in southern (O □ Δ) and central (O □ Δ) Norway.

O O Spruce forest with *Vaccinum myrtillus*
Δ Δ Spruce forest with low ferns
□□ Spruce forest with low herbs and grasses

The impact of differences in soil acidification on metal uptake in plants is indicated by the results shown in Fig. 6. The aluminum content in *Anemone nemorosa*, which is localized to the eutrophic spruce forests, is higher in southern Norway, whereas *Calluna vulgaris* from oligotrophic pine forests shows similar concentration in both regions. These results correspond closely to the pattern for aluminum in soil extracts discussed previously. The values obtained for manganese in the same two species show a relative depletion of Mn in southern Norway for species growing on very acidic soil. These values seem to support the trend exhibited for manganese in the gradient study of subproject A.

From the results presented in this paper it seems that the plant uptake of some metals depends significantly on soil acidification. Further work on this project will include additional minor and trace elements.

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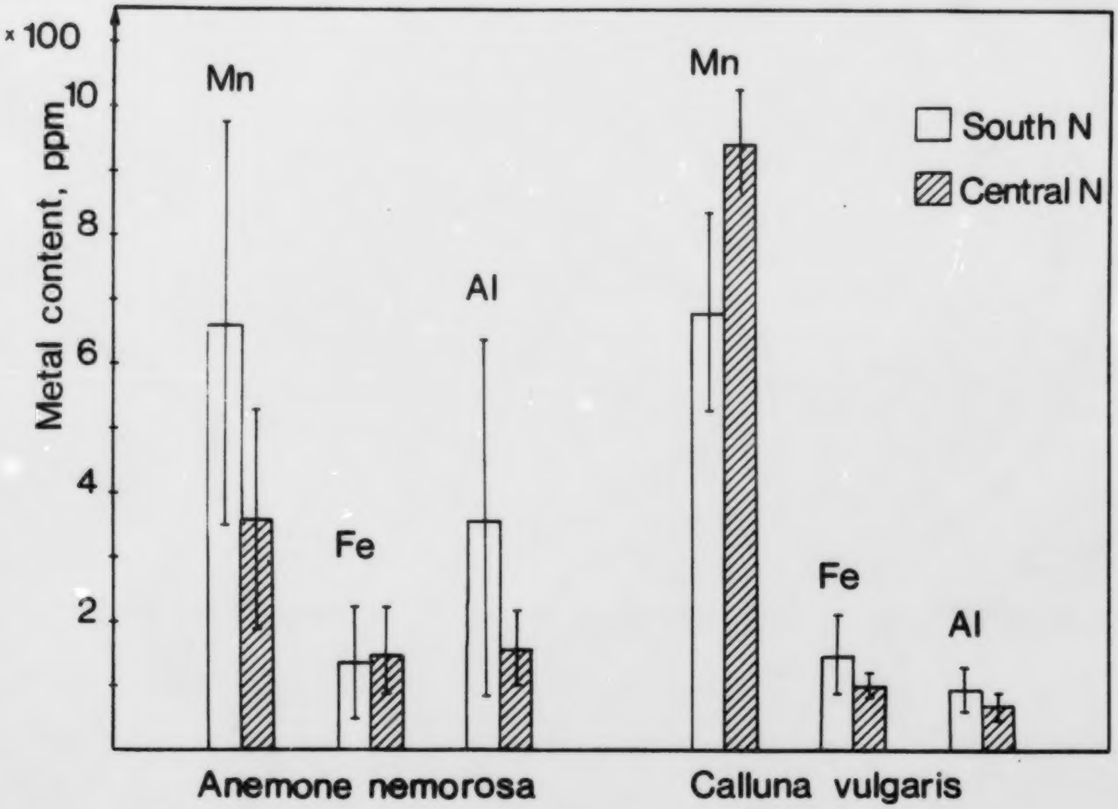

Figure 6. Metal uptake in wood anemone (*Anemone nemorosa*) from eutrophic spruce forests and heather (*Calluna vulgaris*) from oligotrophic pine forests in southern and central Norway.

Direct and Indirect Acid-induced Changes in Foliar Chemical Content

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ABSTRACT

Acid deposition may invoke changes in chemical content of plant foliage. Although acid rain is known to accelerate the leaching of plant substances from foliar surfaces, it is not known whether such changes occur (directly) at foliar surfaces or indirectly through soil acidification. Such modifications may disturb forest element cycles, e.g., nitrogen. Pinto beans (*Phaseolus vulgarus* L.) were grown under greenhouse conditions for 70 days. The soil used was collected from Whiteface Mountain in the Adirondack region of northeastern New York State. Plants received 50 ml of distilled water three times weekly for 63 days. Thirty days after planting, plants received the same volume of synthetic acid rain adjusted to pH 2.5, 4.0, and 5.5 depending on treatment. Synthetic acid rain was prepared by adding dropwise a solution of 60% H_2SO_4 and 40% HNO_3 until the desired pH was obtained. The method of administering rainfall varied according to treatment. Treatment I received rain by means of an air atomizer and the rain was allowed to percolate into the soil. Treatment II received rain by uniform application to the soil surface without wetting the foliage. Treatment III received rain as in Treatment I but the rain was prevented from entering the soil directly by a plastic skirt applied during rainfall periods. Treatment III also received an additional 50 ml distilled water applied directly to the soil as in Treatment II to prevent desiccation. Six plants from three different pots were harvested at regular intervals over a 63-day period for plant tissue analysis. Leaves were separated from the remainder of the plant and analyzed for Al, Ca, Mg, K, Mn, and total N. Results suggest there are differences in elemental concentrations of plant foliage among treatments. Differences varied with the pH of the simulated rain and the elements studied. No general trends for all elements were obvious.

INTRODUCTION

Acid deposition may invoke changes in the chemical content of plant foliage. It is known that acid precipitation accelerates the leaching of plant substances from foliar surfaces (Wood and Bormann 1974). It is not known, however, if changes in the chemical content of plant tissue occur directly at foliar surfaces or indirectly by means of soil acidification (with subsequent changes in nutrient uptake patterns) or whether the changes are a result of both these processes.

Modification of foliar chemical content in a forested system may disturb forest element cycles, e.g., nitrogen and calcium. Changes in foliar elemental content also may impact forest consumers and increase or decrease the probability of insect infestation. Decomposition may be retarded because of changes in litter substrate quality; forest productivity also may be altered. Similar changes in the foliar chemical content of agricultural crops destined directly for human consumption or indirectly by way of agricultural food chains are also possible. These changes have serious implications because decreased nitrogen content may result in lower protein content and decreased nutritional value.

The mechanism by which foliar chemical content is modified must be elucidated because remedial measures should be selected recognizing the perturbation mechanism. If the mode of action is direct through chemical leaching, one set of management alternatives is suggested. If the mode of action is indirect and foliar chemical content is modified as a result of soil acidification and subsequent changes in nutrient uptake patterns, then additional management alternatives become available. Since changes in productivity and substrate quality are of vital importance, the mechanism by which these changes occur must be known.

MATERIALS AND METHODS

Pinto beans (*Phaseolus vulgaris* L.) were planted in 10-cm plastic pots with two plants per pot. Soil was collected from Whiteface Mountain in the Adirondack region of northeastern New York State. Plants were placed in a greenhouse and grown under natural lighting conditions. Plants received 50 ml tap water three times weekly. After 42 days, plants received the same volume (50 ml) of synthetic "acid rain" adjusted to pH 2.5, 4.0, or 5.5 depending on treatment. The synthetic acid rain was prepared by adding dropwise a solution of 60% H_2SO_4 and 40% HNO_3 until the desired pH was attained. The method of administering rainfall varied according to treatment. Treatments are depicted in Figure 1. Treatment I (direct and indirect effects) received rain by means of an air atomizer and the rain was allowed to percolate into the soil. Treatment II (indirect effects only) received rain by uniform application to the soil surface without wetting the foliage. Treatment III (direct effects only) received rain by means of a sprayer. The rain was prevented from entering the soil by application of a plastic skirt during rainfall periods. Treatment III received additional distilled water (50 ml) adjusted to pH 5.5 and applied uniformly to the soil surface to prevent desiccation.

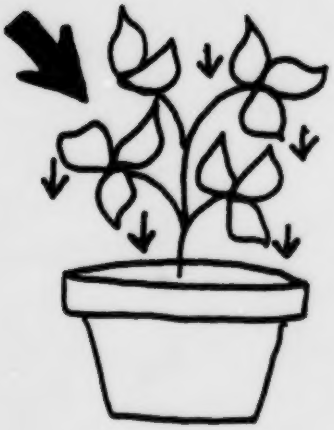
Three different pots (six plants) were harvested from each treatment at day 44, 58, and 63 for tissue analysis. Leaves were separated from the remainder of the plant, dried at 40°C, weighed, then ground in a Wiley Mill to pass through a 2-mm mesh screen. Sample aliquots were dry-ashed (Allen et al. 1974) for analysis of Al, Ca, Mg, K, and Mn and acid digested for total N analysis (EPA 1974). Cation concentrations were measured using an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

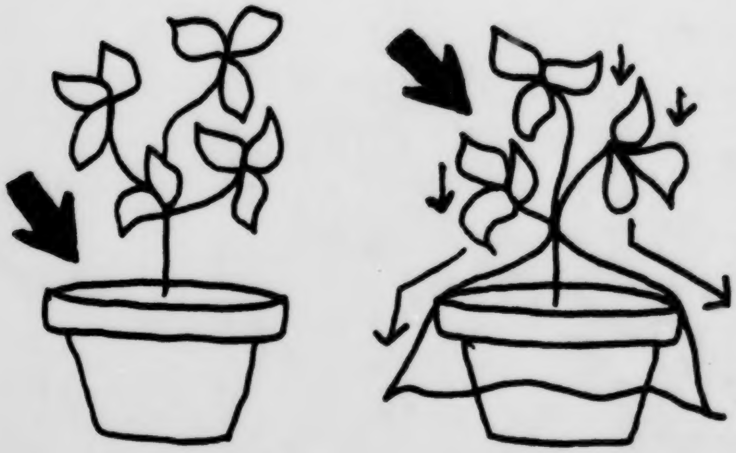
Plants receiving simulated rain at pH 2.5 in Treatments I and III developed foliar lesions after one week of application. Lesions, initially appearing on leaf edges, increased in size and number with increasing exposure time. No foliar damage was observed for plants receiving simulated acid rain at pH 2.5 indirectly (Fig. 1, Treatment II), or for plants receiving simulated rain at pH 4.0 or 5.5.

Total leaf biomass decreased with increasing acidity and was more pronounced in Treatment I (Fig. 2) and III (Fig. 3). Some fertilizing effect may be evident in Treatment I at pH 4.0. This increase in biomass may have been induced by sulfate or nitrate additions. The data for Treatments I and III suggest that total biomass is more influenced by a direct/indirect mechanism. This suggests that indirect effects of acid precipitation may play a role in determining productivity.

Total N values were higher in Treatment I at all pHs (Fig. 4). This suggests that the direct and indirect effects together may be more important than the separate effects in the regulation of total N content, especially at lower pH.



Treatment I
(Direct & Indirect Effects)



Treatment II
(Indirect Effects)

Treatment III
(Direct Effects)

Figure 1. Diagrammatic representation of experimental design.

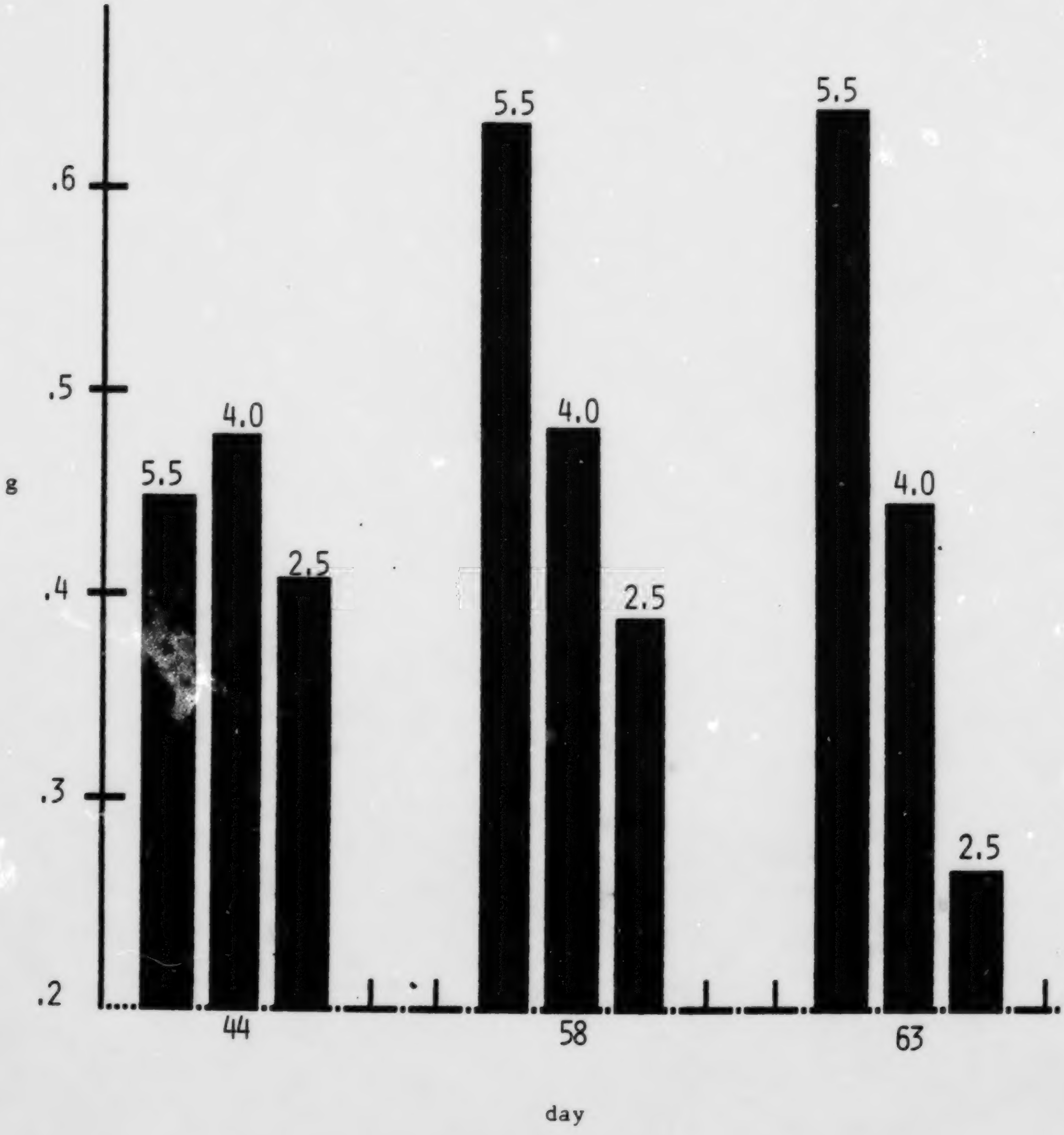


Figure 2. Total leaf biomass, Treatment I at three pH levels.

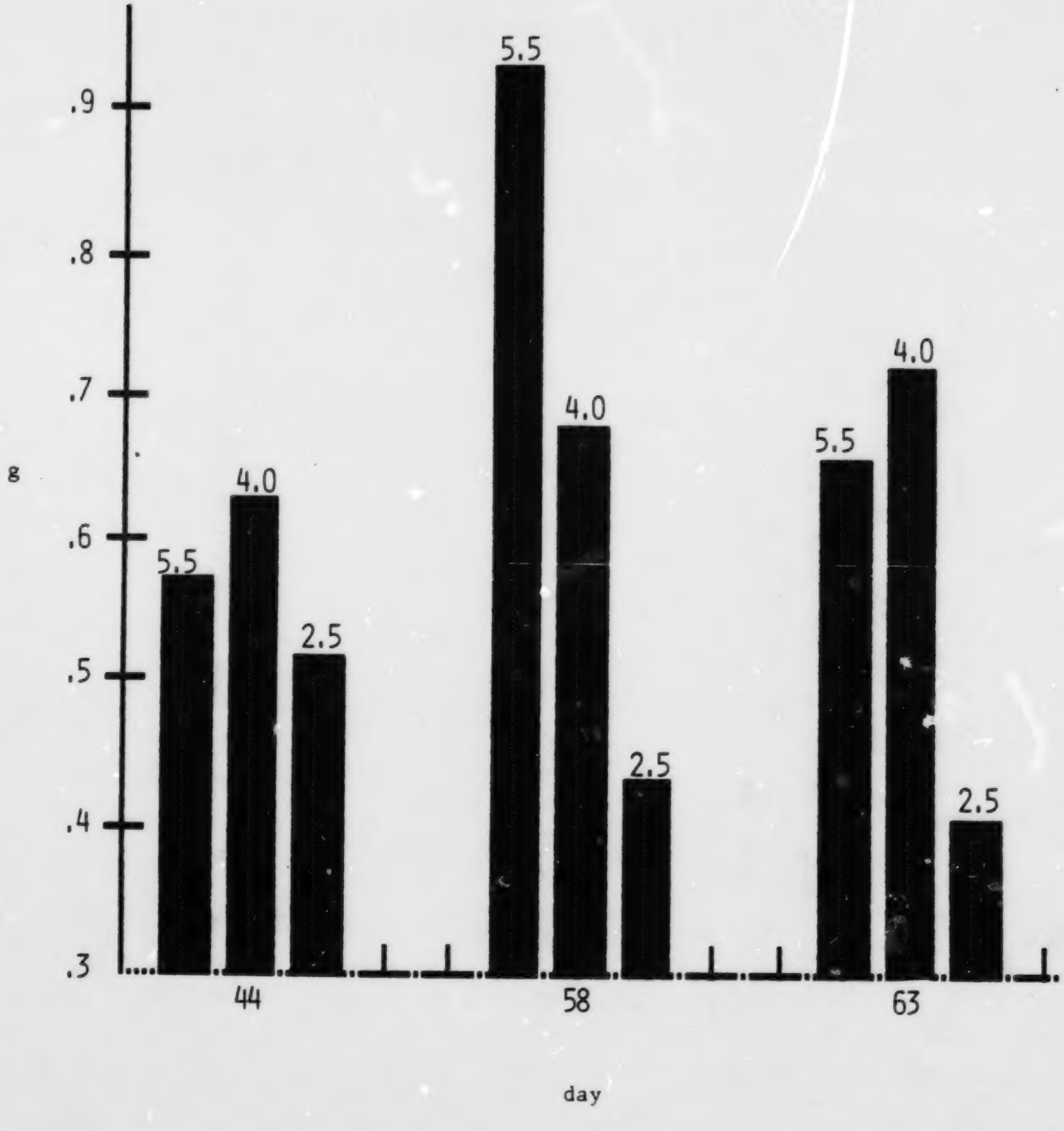


Figure 3. Total leaf biomass, Treatment III at three pH levels.

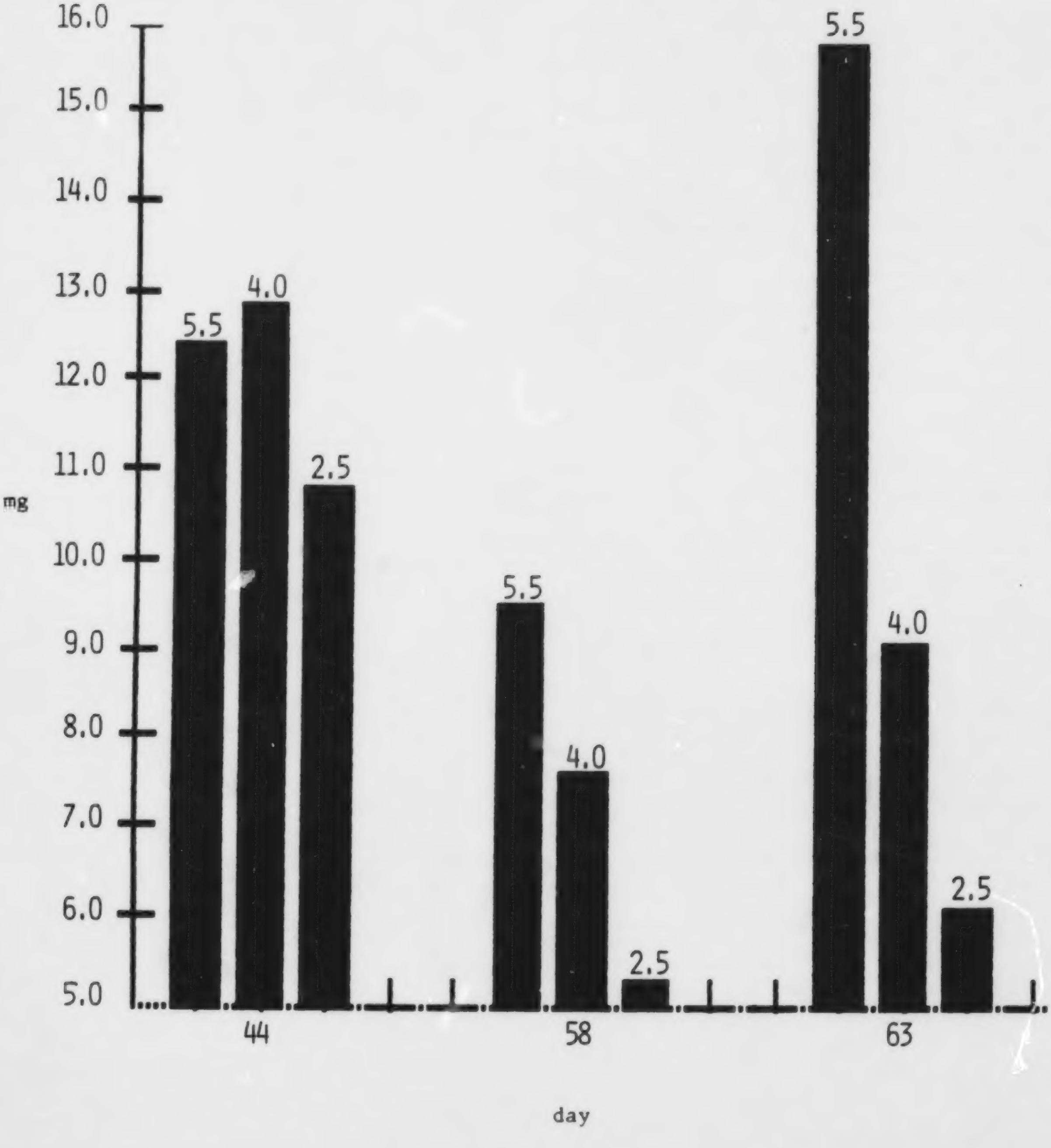


Figure 4. Total leaf nitrogen, at three pH levels.

Assuming a nitrogen-limited system, as one might expect using soils obtained from Whiteface Mountain, some fertilization effect might be anticipated. Stimulation of growth also would be evident in data for other elements. The Treatment I potassium data (Fig. 5) indicate that, at pH 5.5, the elemental content remained fairly constant at each sampling period. At pH 2.5, however, two factors came into play: fertilization and foliar injury. In Treatment I (direct and indirect effects combined) foliar injury occurred in conjunction with the fertilization effect (Fig. 5). At the first sampling period, foliar injury was not great but, over time, as injury became more severe, K content decreased. This was in contrast to Treatment II (Fig. 6, indirect effects) where no foliar injury occurred and only the fertilization effect was observed. In this case, K content increased. Recovery of total N concentrations after fruiting was less pronounced in plants receiving lower pH-rain. Treatment II appeared most affected with no recovery evident at pH 2.5.

Magnesium and manganese were not considered macronutrients and, because of this, changes in tissue concentrations were less dramatic. Aluminum analyses were also performed on the tissue samples but aluminum was not detectable with the digestion procedure employed.

During the first sampling period (44 days), Ca showed some variation among the different treatments and pHs, but no obvious injury or effects were evident. During the second sampling period (58 days), however, pH appeared to have a negative effect in all treatments, i.e., Ca content decreased with increasing acidity. During the third sampling period (63 days, Fig. 7), an effect similar to potassium was observed. In this case, there was a decrease in Ca content in Treatment I, suggesting the negative acid effect, and an increase in Treatment II, indicative of the positive fertilization effect. Treatment III shows inconclusive results with an apparent negative effect at pH 2.5 but a stimulatory effect at pH 4.

Research in this area poses many challenging questions concerning the dose-response relationship of vegetation to low-pH simulated rain. It is not known to what extent leaf surface interactions may alter nutrient cycling within the plant. It is also not known whether direct and indirect effects combine to produce the total observed effect or if a positive fertilization effect occurs in conjunction with negative foliar injury. In addition, it is not known how this mechanism might change at different levels of acidity. Further investigations are designed to examine these interactions in greater detail.

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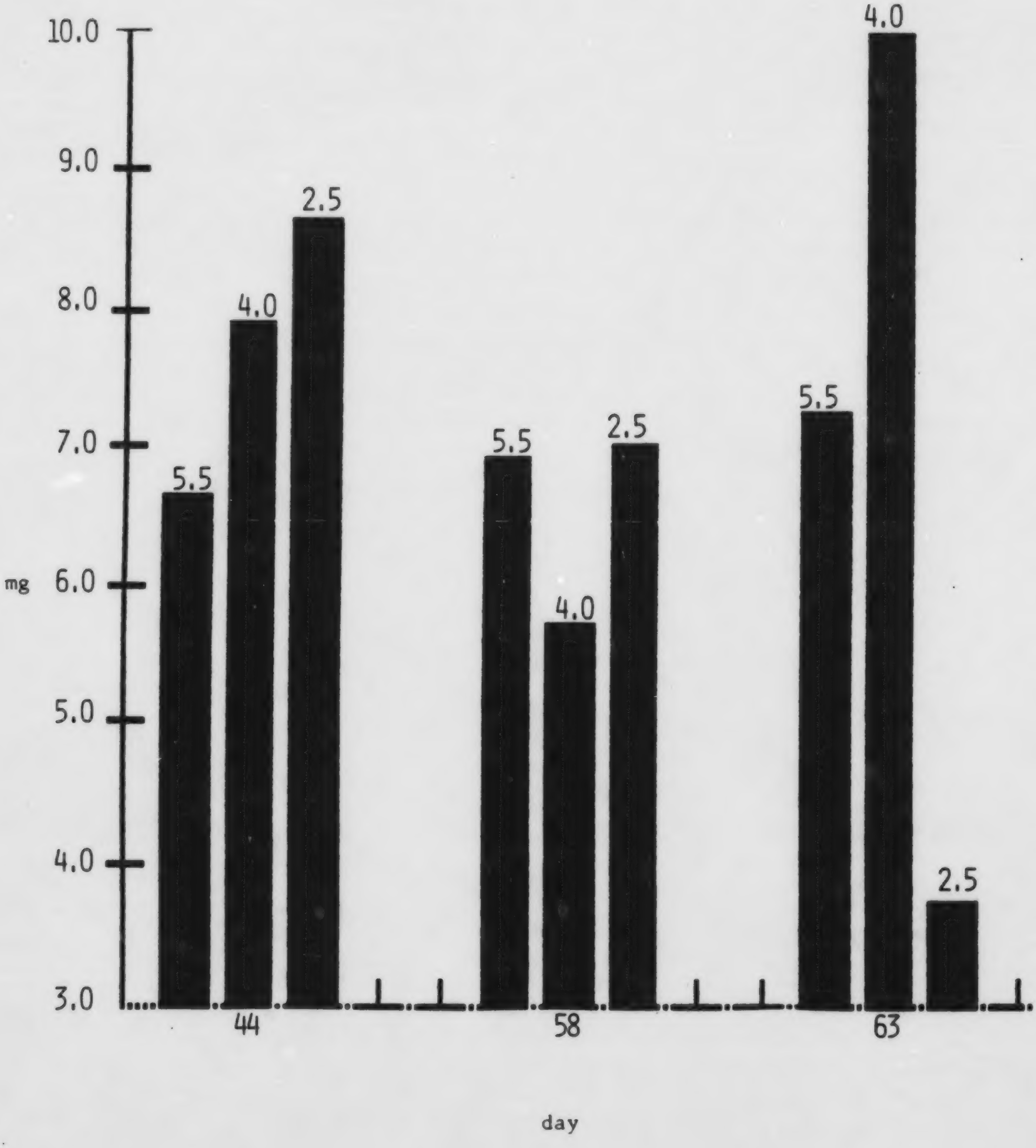

Figure 5. Total leaf potassium, Treatment I at three pH levels.

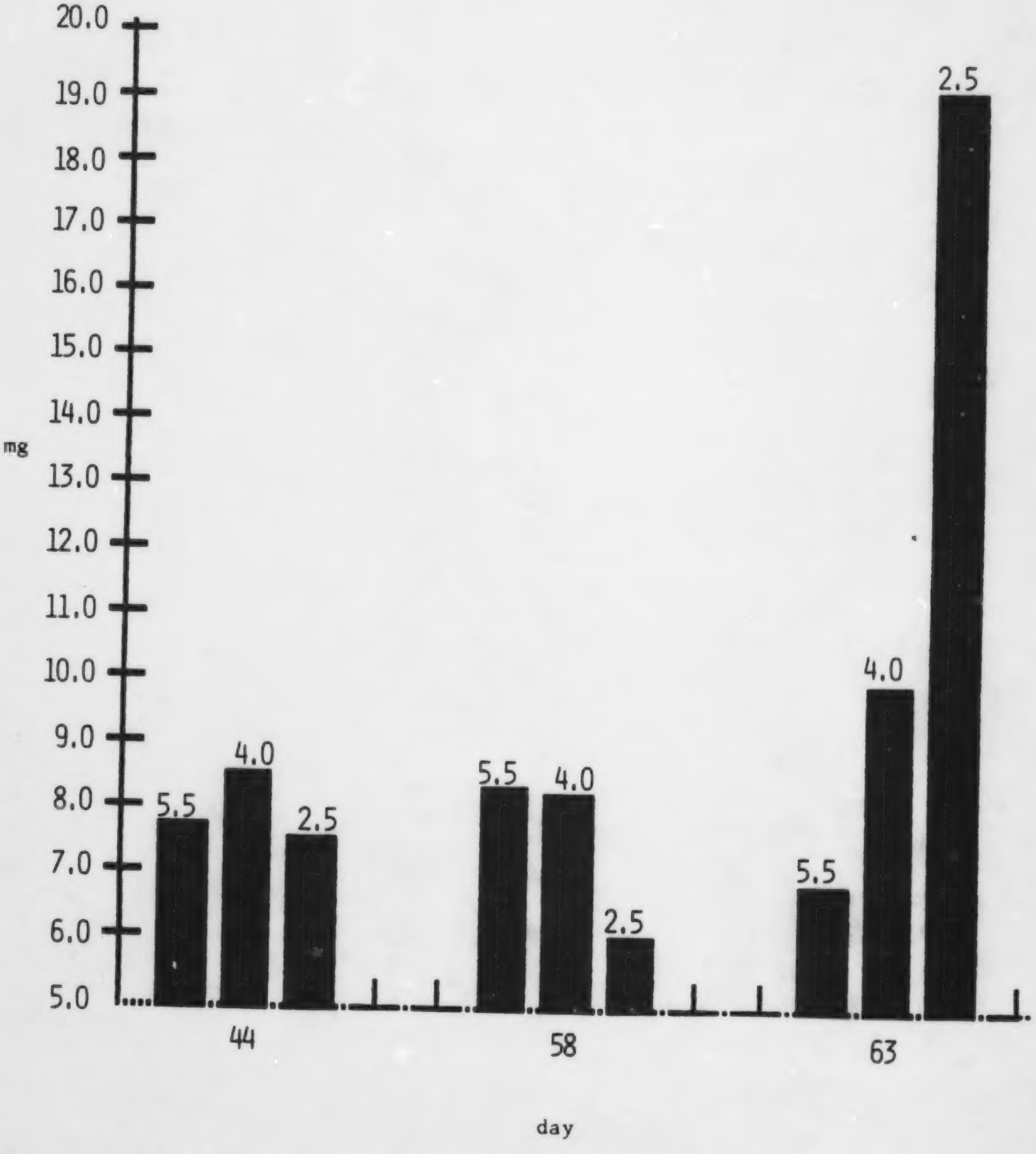

Figure 6. Total leaf potassium, Treatment II at three pH levels.

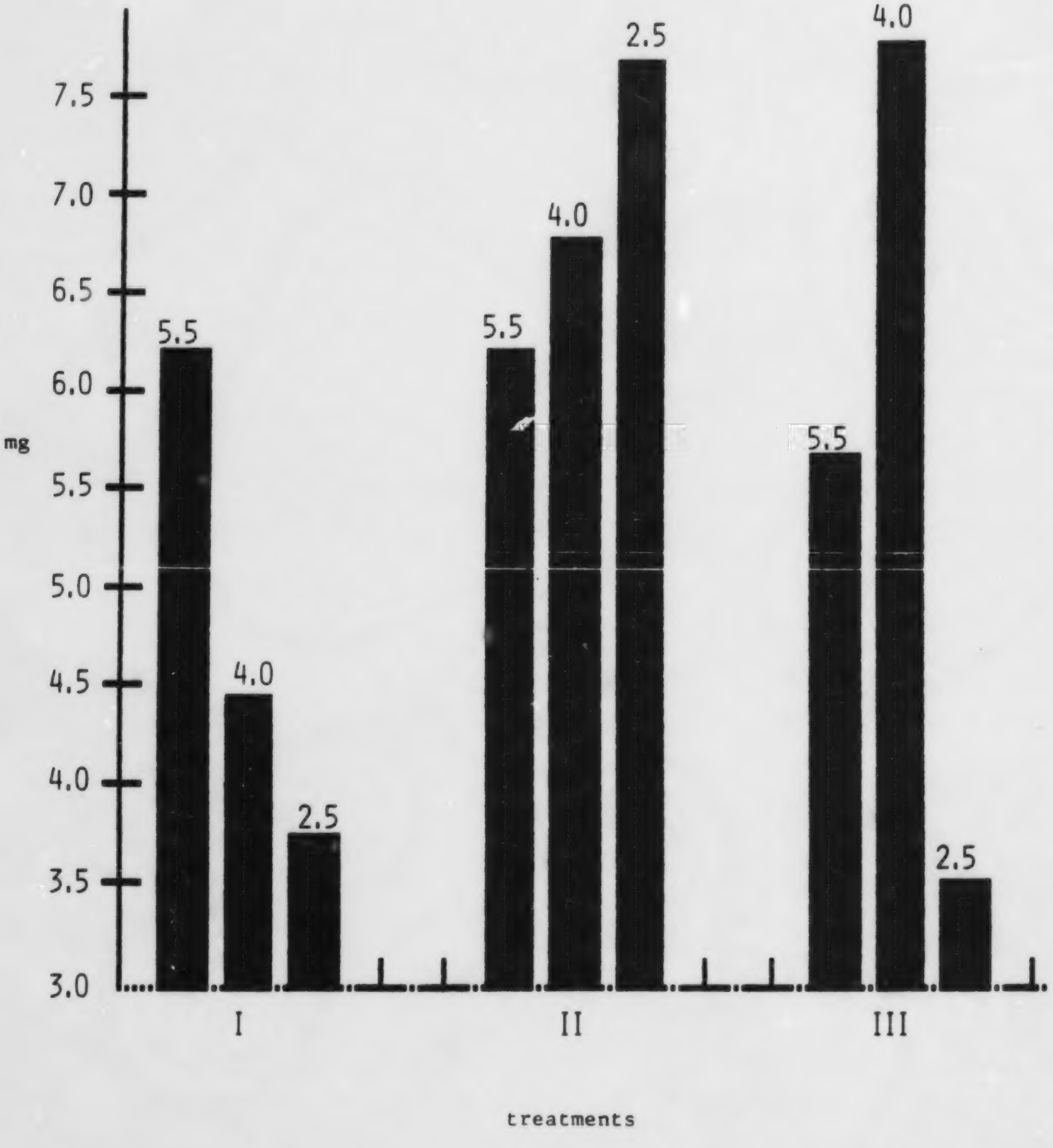

Figure 7. Total leaf calcium, day 63 at three pH levels.

Changes in Acid Flux Through Forest Canopies

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INTRODUCTION

It has long been established that considerable alterations occur in the chemistry of rainwater as it passes through a forest canopy. Most observations suggest a loss of acidity and an increase in base cations (e.g. Eaton et al. 1973), changes that vary with the pH of incident rainfall (Horntvedt et al. 1980) and which are due, at least in part, to hydrogen ion exchange at leaf surfaces. Further interpretation is confused by the fact that rainwater, as well as gaining elements derived from within the plant (crown leaching), also washes from the surface of the leaves those salts and other substances that have been filtered from the atmosphere through turbulent transfer and impaction (interception deposition). Ulrich (1983) suggested that true crown leaching from healthy tissues is essentially limited to hydrogen ion exchange for calcium and magnesium on cell walls and to the acquisition of potassium and manganese resulting from metabolic processes. He considered that 90% or more of the sodium, chloride and sulphate enriching rainwater passing over trees is derived from interception deposition. Other authorities, however, would be reluctant to accept that there is little or no leaching of sulphate from plant tissues. Experimentation is difficult and published results suggest that much depends on the method of assessment employed. Certainly, a large proportion of the sulphate gain beneath trees in polluted areas must be derived from intercepted SO_2 and related gases. However, the fact that $^{35}SO_4$ can be shown to be moderately easily leached (Tukey et al. 1958) indicates that leaching could contribute to the sulphate in throughfall. Parker (1983) has recently concluded, from a wide-ranging review of the literature, that in unpolluted areas foliar leaching may account for more than half the gain of sulphate.

Thus, there is still no clear understanding of the factors controlling exchange of acidity in forest canopies, nor of their relative importance in different situations. From the results available it seems that the extent of hydrogen ion loss from rainwater may vary appreciably both with age of tree and with species (Miller in press). Here we report results from a study of rainwater acidity beneath a range of vegetation types and also present evidence for a seasonal variation in rainwater acidity beneath trees in polluted areas.

SEASONAL EFFECTS

The change in pH of rainwater as it passes through the forest has been monitored over five years in replicated plots of unfertilized and fertilized Sitka spruce (*Picea sitchensis* (Bong.) Carr.), aged 25 to 30 years, in each of six locations chosen to cover the bioclimatic conditions encountered in Scotland and northern England. These sites ranged from extremes of a relatively unpolluted area at Leanachan forest, near Fort William, on the north-west coast of Scotland, to Fetteresso forest, south of Aberdeen, on the east coast and, in the prevailing south-westerly airstream, downwind of much of industrial Britain. Over the five years, 1973-78, pH of bulk deposition averaged 4.54 at the former site and 4.13 at the latter.

In addition to bulk deposition, which was collected in a Nipher-shielded gauge, water was collected in funnels surmounted by a vertical cylinder of polyethylene-coated wire mesh. This mesh acted as an inert surface to collect some fraction of the interception deposition, a deposition that would be subsequently washed down into the funnel in rainwater (Miller and Miller 1983). The average pH in the water collected by these "filter gauges" was 4.81 and 3.92 at Leanachan and Fetteresso, respectively. Thus, at Leanachan interception deposition had a notable neutralizing effect whereas at Fetteresso there was a slight acidifying effect. Slight decreases in acidity were recorded at two of the other sites (pH 4.3 rising to 4.5 and 4.1 rising to 4.2) whereas at another there was little change (pH 4.2 in both collectors) and at the remaining there was a barely perceptible decrease (pH 4.46 to 4.40). At most sites average pH of throughfall was higher than that of bulk deposition, whereas average pH of stemflow was lower. The extremes are again represented by Leanachan, where pH of stemflow was the same as that of bulk deposition, and by Fetteresso, where throughfall pH showed no change from that of bulk deposition.

These long-term means hide considerable annual variation, particularly at Fetteresso. In order to examine this the pH values for approximately monthly collections (disturbances to the regular sampling pattern largely resulted from access problems during winter) were subjected to repeated curve fitting, in segments of nine points, advancing one point at a time, to derive, by weighted averages, estimated values at precisely four-week intervals. Fourier analysis was then carried out using these derived values and the significant harmonics revealed were tested against the original data points. Those harmonics that made a significant contribution to explaining the variation in the original data were together solved to produce fitted curves such as those shown in Figure 1. Streamwater data were derived from spot samples collected at approximately two-week intervals, with exact fortnightly points being interpolated as described above.

At neither Leanachan nor Fetteresso were there any marked annual variations in the pH of either bulk deposition or the water collected in the filter gauge. Indeed, at Leanachan the only suggestion of an annual feature was the low winter pH in streamwater, reflecting the winter spates in the fairly substantial stream that drains this experimental area. At Fetteresso the stream is no more than a small drain and no annual pattern in pH is evident. However, at this site there are clear annual variations in the acidity of both throughfall and stemflow, although the patterns for these two components of net rainfall appear to be slightly displaced. If converted to hydrogen ions there is then marked episodicity in the flux of acidity to the soil surface, ranging from a maximum of about 30 g H^+ ha^{-1} wk^{-1} in March to only 2 or 3 g from mid-May until early October (Miller 1983).

When examined across all six experimental sites it is clear that this pattern of an annual oscillation in throughfall and stemflow pH develops and intensifies with decreasing average pH of incident rainfall. So far no effect of soil or physical climate has been identified.

EFFECTS OF SPECIES AND AGE

At Glen Tanar forest, some distance inland from Fetteresso, an intensive study was carried out over two years of the changes in pH of water as this drained through the tree canopy, ground vegetation, humus and mineral soil in a range of vegetation types. These were selected to represent alternative forms of hill-land use in northern Europe. Thus, replicated plots were laid out in old (110-year-old) open *Pinus sylvestris* L., fully-stocked young (45-year-old) *P. sylvestris* L., intensively managed *Picea sitchensis* and *Larix kaempferi* (Lamb.) Carr., naturally occurring *Betula* (predominantly *pendula* Roth.) and fire-maintained heaths of almost pure *Calluna vulgaris* L.

Over the full period of study all tree canopies, except that of the old *Pinus sylvestris*, reduced acidity in throughfall. The acidity was further reduced on passing through the ground vegetation, only to be regenerated in the humus layer and decreased again on passing through the mineral soil (Figure 2). At every stage, however, there are marked differences between the crops studied, a striking feature being the consistently acid waters below the old *Pinus sylvestris*, a feature that distinguishes it even from the young crop of the same species. It is not clear why age should have such a marked effect, although in a survey of the available literature Miller (in press) subsequently noted a consistent tendency for older conifers (> ca. 60 years) to acidify throughfall, whereas both younger conifers and broadleaved species seem equally effective at reducing throughfall acidity.

Vegetation induced reductions in acidity are most pronounced in summer, even for evergreen species (Figure 3), the converse being that acidification, where it occurs, is most pronounced in winter, a variation that reflects the pattern of neutralisation and acidification noted earlier at Fetteresso (Figure 1).

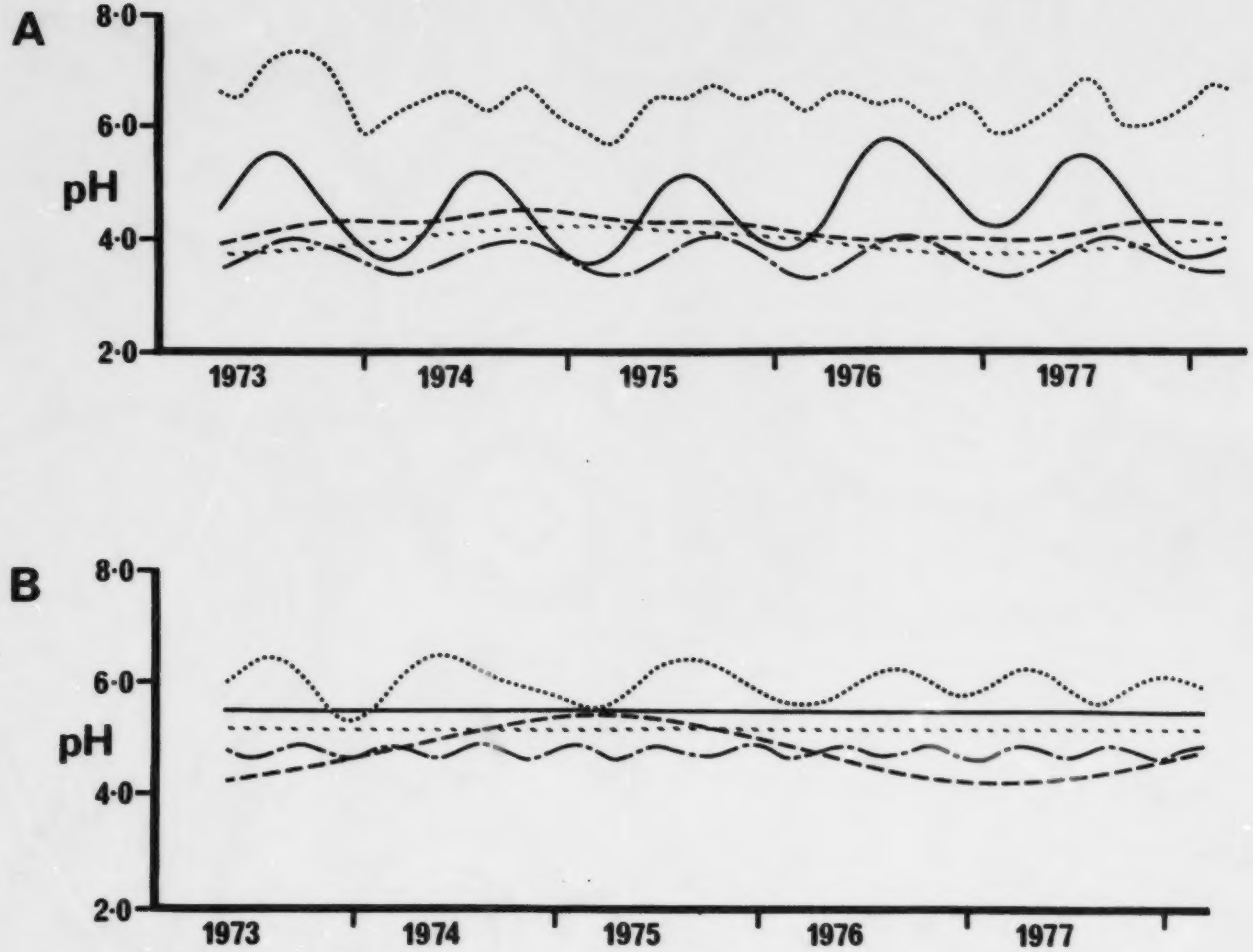

Figure 1. Variations (A) at Fetteresso forest, on the Scottish east coast, and (B) at Leanachan forest, on the relatively unpolluted west coast, in pH of bulk deposition (— — — —), water collected in the "filter gauge" (------), throughfall (————), stemflow (--———--) and streamwater (.............) measured over the five years 1973-78 in crops of *Picea sitchensis*.

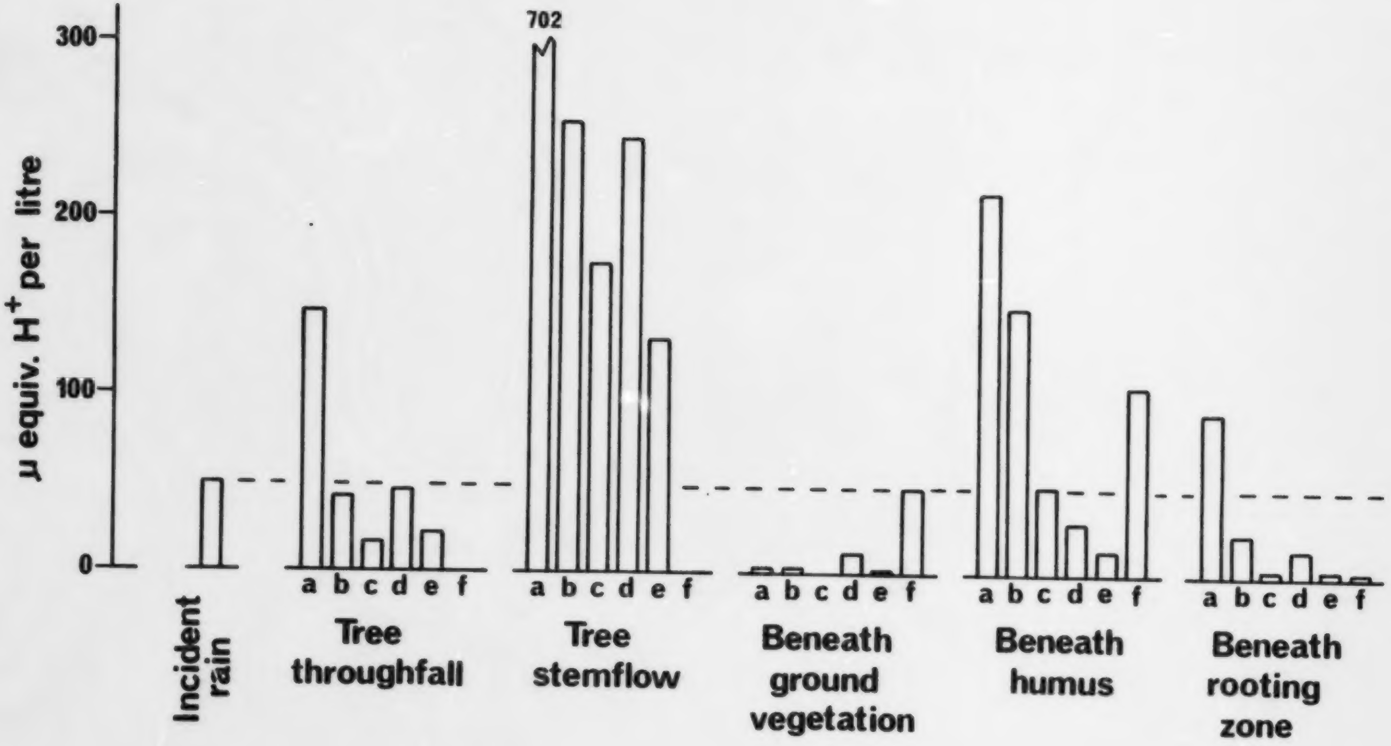

Figure 2. Mean H + concentration in water collected at various points on its passage through the ecosystem for crops of (a) 110-year-old *Pinus sylvestris*, (b) 45-year-old *Pinus sylvestris*, (c) *Picea sitchensis*, (d) *Larix kaempferi*, (e) *Betula* spp. and (f) *Calluna vulgaris* heath at Glen Tanar forest.

POSTCRIPT

Before definite conclusions can be drawn much more information is required, particularly about the processes that lead to chemical changes in rainwater as it passes over vegetation. It could be considered that these canopy effects are of little significance, in so far as the loss of acidity in the crowns represents no more than a transfer of the acid stress to the soil, from which the neutralising cations have originally been derived. However, the appearance of regular fluctuations in throughfall and stemflow pH suggests that tree crowns may have a role in damping the impact of sudden incursions of acidity. Furthermore, the recorded variations with species and age seem to counsel caution over explanations that concentrate on anthropogenic sources, at the expense of physiological factors, in discussions of the cycle of acidity within ecosystems.

ACKNOWLEDGEMENTS

The study at Glen Tanar was by kind permission of the owners and was sponsored by the Central Electricity Generating Board. Permission for the studies at Leanachan and Fetteresso was given by the appropriate Conservators of the Forestry Commission who also provided valuable assistance in maintaining the experiments.

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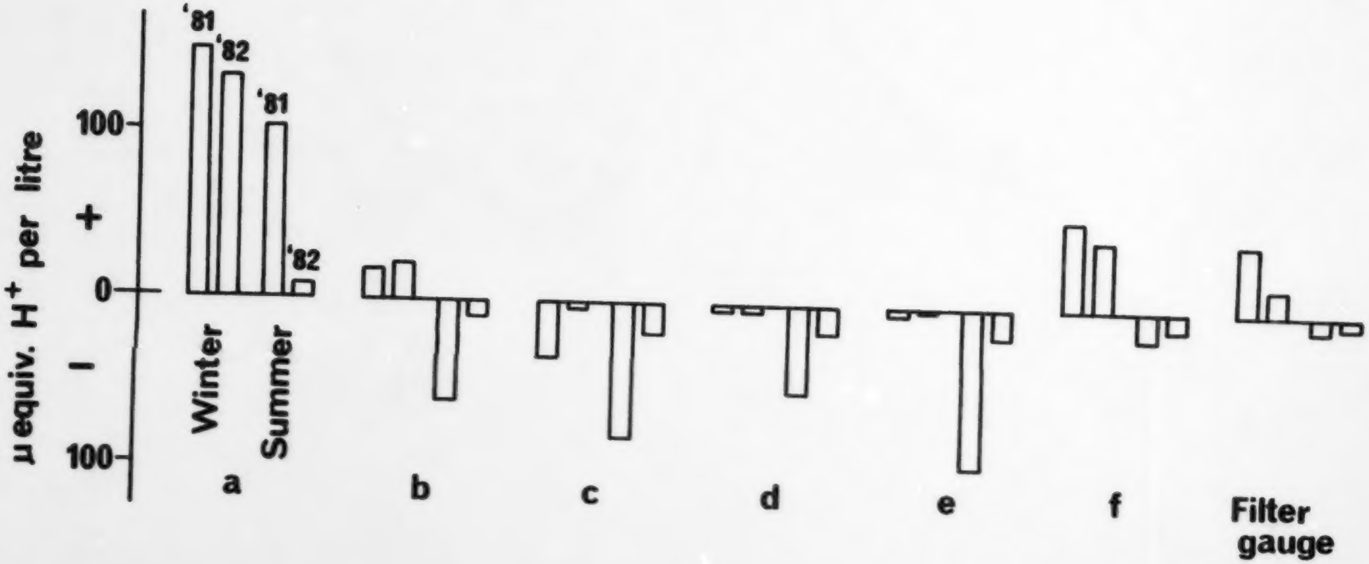

Figure 3. Difference in H + concentration between throughfall and bulk precipitation, by seasons, in 1981 and 1982 at Glen Tanar forest, beneath (a) 110-year-old *Pinus sylvestris*, (b) 45-year-old *Pinus sylvestris*, (c) *Picea sitchensis*, (d) *Larix kaempferi*, (e) *Betula* spp., (f) *Calluna vulgaris* heath, (g) the inert interception surface of the "filter gauge".

Significance of Nutrient Cycling Processes in Forest Ecosystems in Altering Acid Rain Effects

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ABSTRACT

The effects of acid rain on terrestrial ecosystems can often be explained in terms of its influence on various nutrient cycling processes. The ecosystems, being dynamic and resilient, can be expected to have mechanisms to buffer acid rain effects. Such resiliency can vary among different ecosystems depending upon their components and their ability to counteract or withstand perturbations. In this report, some of the discernible influences of tree species in altering acid rain effects are discussed. Nutrient cycling studies were started during the early 1970s in six softwood and three hardwood stands located at the Acadia Forest Experiment Station in central New Brunswick. From the data obtained, there are at least four distinct species-dependent processes that appear to alter acid rain effects. These processes include (a) partitioning of rain water, (b) exchange reactions of nutrients at the plant (leaf and bark) surfaces, (c) building up of organic matter (humus) horizons under the stands, and (d) exchange reactions within the organic horizons. The relative significance of each of these processes in altering acid rain effects in different stands is discussed.

INTRODUCTION

More than 30 proceedings of ecological conferences have been published since 1981. A majority of these deal with the cycling of nitrogen, carbon, sulfur, and phosphorus in terrestrial ecosystems. One common theme in most of the articles is the need to carry out process-oriented research. Some of the processes characterized in a few forest ecosystems at the Acadia Forest Experiment Station (A.F.E.S.) in central New Brunswick are presented here to show that they have an ability to counteract acid rain effects.

This report is based on some of the data gathered in three hardwood and six softwood stands during the past 13 years. Using data on the chemical characteristics of rain, stemflow, throughfall, stand and soil systems, the abilities of different stands to alter rain acidity are described. Interactions between precipitation and various components of forest ecosystems can be explained in terms of four processes. These processes are species-dependent and influence the degree to which rain acidity is altered. They are:

a) partitioning of rain water
b) exchange reactions between tree components and rain water
c) buildup of humus layers — thickness and weight of organic matter
d) moisture retention and absorption affecting the exchange reactions between organic compounds in the soil and various chemicals in the stemflow and throughfall liquid.

The first two processes occur in the forest canopy before precipitation reaches the ground, whereas the latter two are controlled by the organic and mineral soil horizons.

METHODS AND PROCEDURE

The data reported here were gathered over a number of years, and the information regarding methods employed in various studies has been published earlier. Methods describing the collection and processing of precipitation, throughfall, and stemflow can be found in reports of Mahendrappa (1974, 1983) and Mahendrappa and Kingston (1982). Another publication by Mahendrappa and Kingston (1980) contains data on the weights and thickness of organic horizons under different stands.

Moisture retention curves for individual (L, F, and H) horizons were obtained through a method using a pressure plate apparatus (Richards 1965). Moistening of the organic horizon materials before transferring them to pressure plates was necessary to ensure complete wetting of the samples. The moisture retained in the samples was determined after exposure to a pressure of 33 kPa for 48 hours. This value was considered to represent the field capacity (or the water-holding capacity) of the organic horizons.

RESULTS AND DISCUSSION

The precipitation passing through the forest canopy is partly intercepted (I) and returned to the atmosphere through evapotranspiration. Part of the rain water reaches the ground as stemflow (S.F.) whereas the remaining portion of the rain water reaches the ground as throughfall (T.F.). Throughfall, for the most part, comes in contact with some tree part during the process of falling to the ground. Such partitioning of water can be represented by an equation

$$P = S.F. + T.F. + I$$

During the course of our study the proportion of rain reaching the ground as stemflow was generally less than 5% (Mahendrappa 1974). The contribution of stemflow did not vary much between years. Thus, the observed percentage values were used to calculate the volume of stemflow for different species from rain measurements made in the open areas near each stand. Throughfall quantities were found to vary linearly with total precipitation. The rectilinear relationship was expressed by the equation:

$$Y = aX + b$$

where

Y = throughfall (mm)
X = total precipitation (mm), and
a and b are species-specific constants.

When the quantities of throughfall are plotted against rainfall quantities we can clearly see the effects of tree species (Fig. 1). First, the relationships are rectilinear, and second, the differences between species are clear with respect to the minimum quantities of rain that must fall before throughfall can be collected. Differences in the quantities of rain water reaching the ground are greatest among species when rainfall is less than about 5 mm. All these are well-established facts, but what do they mean in terms of acid rain?

When rainfall is less than 5 mm the tree species that intercepts more precipitation retains more chemicals that cause acidity. Components of both dry and wet deposition are, therefore, able to react longer with the tree components.

Our data show that softwoods intercept more rainfall than hardwoods. In the context of acid rain this means that conifers retain more rain acidity or neutralize less acidity.

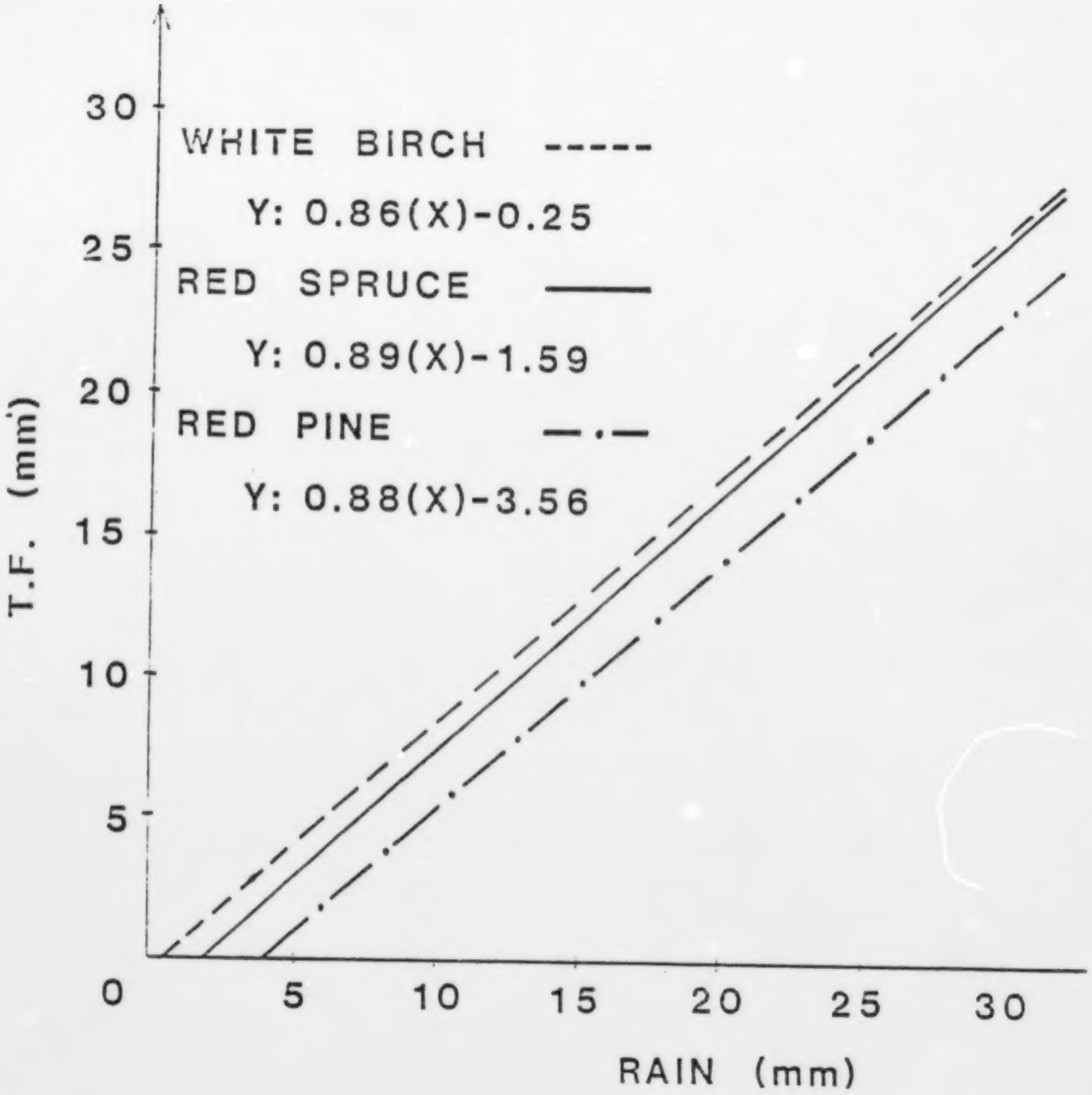

Figure 1. The observed relationships between quantities of rainfall in the open areas and throughfall under some forest stands at A.F.E.S.

It is necessary, however, to take into account another process that occurs on tree surfaces. The chemicals in the rain enter exchange reactions with those in the foliage and bark. Cations from the foliage and bark are invariably leached by rain water. Published data show that the degree of leaching depends, among other factors, on the chemical composition of rain. It is well established that hydrogen ions in rain are exchanged for the cations from plant tissue. This means that the pH of throughfall is invariably higher than that of open rain.

Species differ in their ability to reduce the acidity of rain through exchange processes. The data in Table 1 indicates that the pH of hardwood throughfall is generally higher than that of softwood throughfall. For several reasons, however, the pH data do not allow us to draw conclusions with respect to the differences between hardwoods and softwoods in their ability to counteract acid rain effects: (a) the pH differences may not be large enough to detect species effects (b) the observed pH differences may be due to the fact that hardwoods intercept less rain (c) the trees' ability to neutralize rain acidity depends on the physiological and nutritional status of the trees, and (d) the interval between rain events and the quantity of rain also influences the quantity of rain acidity neutralized by forest trees. Thus, to evaluate the true significance of forest ecosystems the most logical approach is to calculate the quantities of hydrogen in the incident precipitation and that in the throughfall and stemflow of different species (Table 2). The values in the last column of Table 2 clearly indicate that hardwoods neutralize higher proportions of rain acidity than do softwoods. This also means that hardwoods circulate more cations than softwoods in the solution phase.

Table 1. The observed pH of rain, stemflow, and throughfall in some hardwood and softwood stands at A.F.E.S.

	pH		
Species	Rain	T.F.	S.F.
White spruce	4.51	4.99	4.60
Red pine	4.42	4.73	4.61
Balsam fir	4.51	4.64	4.33
Maple	4.35	5.44	5.18
Aspen	4.21	5.45	6.16

Table 2. Average quantities of hydrogen (equivalents ha-1) deposited on the forest floor by stemflow, throughfall, and rain, during May-October of 1977-81 at A.F.E.S.

	Hydrogen ion input equivalents ha^{-1}				
Species	S.F.	T.F.	S.F. + T.F.	Rain	Percent H neutralized
Red spruce	23.03	103.16	126.19	235.41	46
Red pine	5.19	113.36	118.55	208.65	43
Maple	2.39	64.14	66.53	219.81	69
Aspen	0.44	43.37	43.81	224.08	80

The third species-dependent process that is capable of counteracting acid rain effects is the buildup of organic or humus horizons under the stands. Acidity is one of several factors that may be responsible for the buildup of organic horizons under different stands. The cause-effect relationship of organic matter buildup under different conditions is a complex process and not well understood. However, buildup appears to be a process capable of altering acid rain effects. In the first three columns of Table 3 the weights of individual organic horizons under different stands are given. As can be seen, values differ. The values in column 4 represent the sums of the data obtained for individual (L, F, H) horizons. These stands are generally of the same age and have similar densities. Thus, the weight differences in the organic horizons can be attributed to species effects.

Table 3. Weights (1000 kg ha^{-1}) of organic horizons under different stands at A.F.E.S.

Species	Horizons L	F	H	Total
Red pine	13.0	16.1	24.2	53.4
Red spruce	15.0	27.4	40.0	82.5
Maple	6.3	14.0	30.6	50.9
Aspen	12.9	53.9	72.9	139.0

It is relatively easy to calculate the proportion of rain intercepted by the canopies because the quantity of fluid can be accurately measured before and after interception takes place. Because this is not possible with respect to the organic horizons, a different approach is employed. The amount of water that can be retained under field conditions is estimated using a porous pressure plate apparatus. The values determined (Table 4) show that there are significant differences among quantities of water retained at field capacity by individual organic horizons under different tree species. The species effect is also clearly evident with respect to the total quantity of water retained by the organic humus (L + F + H) horizons under different stands. Again, as is the case with the forest canopies, differences among species in the quantity of water retained by the organic horizons can be greater when rainfall is less than 20 mm. Up to a certain point, all the stemflow and throughfall reaching the ground can be retained by the humus horizons. This, however, depends on the degree of dryness of the surface organic horizon. Extreme dryness creates hydrophobic surfaces that result in water repellency. Thus, different tree species affect, among other factors, the buildup of organic horizons which, in turn, determine the quantity of water retained under different stands.

Table 4. The average quantities (mm) of water retained at field capacity by different organic horizons under different stands at A.F.E.S.

Species	Horizons L	F	H	Total
Red pine	2.9	2.9	3.1	8.9
Red spruce	3.0	3.6	4.3	10.9
Maple	1.2	2.4	4.4	8.0
Aspen	2.2	8.2	10.2	20.6

Various reactions take place between the chemical constituents of stemflow and throughfall liquid and those in the organic horizons; these cause changes in the physico-chemical characteristics of the organic horizon. The pH values of these organic horizons represent the equilibrium levels and indicate, to an extent, the abilities of different organic horizons to alter rain acidity. The higher the pH, the greater the ability of the organic horizon to reduce the acidity of rain. The data in Table 5 clearly show that there are significant differences between the equilibrium pH of different organic horizons under different stands. Thus, the organic horizon under different stands can counteract acid rain effects to different degrees. Cations present in the organic horizons can be another measure of their capacity to counteract acid rain effects. Cation exchange capacity of the organic horizons also differs among stands. Again, the higher the cation exchange capacity and base saturation, the higher the neutralizing capacity will be. The net effect is again dependent upon the total quantity of organic materials, which shows significant differences between stands. The weight of the organic horizons influences the time available for chemicals in the liquid phase to come to equilibrium with those in the organic horizons.

Table 5. pH values of organic horizons under different stands at A.F.E.S.

	Horizons		
Species	L	F	H
Red pine	4.7	4.4	4.3
Red spruce	4.1	3.9	3.7
Maple	5.0	4.7	4.5
Aspen	5.7	5.0	4.4

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The Impact of Acid Rain on the Subarctic Woodland Soils of Eastern Canada

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ABSTRACT

Spruce-lichen woodlands cover about 24 000 km^2 of eastern, subarctic Canada and are underlaid by shallow, acid soils with low nutrient status and slow nutrient cycling. Although most precipitation has pH values > 4.5, significant events with pH < 4.5 have been recorded. Rain passing through the spruce canopy is acidified to pH values of 3.9 to 4.5. To test the effect of increased H^+ deposition on these soils, artificial rain was applied in two 15-mm treatments per week for two summers at pH values of 5.5, 4.0 and 3.0 and with a SO_4:NO_3 ratio of 2:1. Leachates were collected to examine the effect of the treatments on nutrient leaching from the soil. The buffering capacity of the soil is low, with the leachates retaining pH values close to the treatment (4.8-5.0; 4.0-4.3; and 3.0-3.2, respectively). Increased leachate concentrations were recorded in the acid treatments, but total-P concentrations were unaffected. No distinct differences in leachate NH_4^+- and NO_3^--N concentrations were noted, but a laboratory experiment is being conducted to evaluate more thoroughly the impact of acidification on N mineralization. Rates of decomposition and nutrient removal from dead spruce needles and lichen were unaffected by the acid treatments, but decomposition of soil organic matter was reduced by 20% in the pH 3.0 treatment.

Biomass and Macroelements in a Tolerant Hardwood Stand, Turkey Lakes Watershed, Ontario

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ABSTRACT

Data are presented on the distribution of standing-crop biomass and of nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and sulphur (S) by components (foliage, live branches, dead branches, stem bark, stem wood, stumps and roots) in an old-growth sugar maple (*Acer saccharum* Marsh.) -yellow birch (*Betula alleghaniensis* Britton) stand on a shallow, Precambrian-derived acid till soil in Turkey Lakes Watershed, Ontario. The most abundant element in the standing crop was Ca followed by N > K >Mg > S >P. Presented also, for the same site, are estimates made over a 3-year period of annual total litterfall and of the annual cycle of elements from vegetation to soil by this route. The most abundant element in the annual litterfall was N, followed by Ca > K > Mg > S > P. In addition, data are presented on distributions of total organic matter and of elements in the forest floor of the study stand. The order of elements in the forest floor was N > Ca > S > K > Mg > P. The role of litterfall in replenishing bases removed from the soil through plant uptake and leaching is discussed.

INTRODUCTION

In addition to carbon (C), hydrogen (H) and oxygen (O), plants require, for growth and development, adequate supplies of 13 primarily soil-derived inorganic elements. Included are six needed in relatively large amounts, termed 'macroelements': nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and sulphur (S), and seven others needed in lesser amounts, termed 'micro-' or 'trace elements'. In contrast with deficiencies occurring on sites of low supplying ability, situations may exist in which an excess of trace elements is detrimental to plant growth or health. In this latter case, non-nutrient as well as nutrient trace elements may be involved.

The needs of natural vegetation for deficient elements, on the one hand, and the ability of vegetation to cope with conditions of excess, on the other, are both met to a large extent through a complex circulation of elements referred to as the 'biogeochemical cycle'. Rodin and Bazilevich (1967) described this as "the uptake of elements from the soil and the atmosphere by living organisms, biosynthesis involving the formation of new compounds, and the return of elements to the soil and atmosphere with the annual litterfall of part of the organic matter or with the death of the organisms in the biogeocoenosis".

While some writers (e.g., Tamm and Cowling 1976) concerned with the influence on vegetation of pollutants transported over long distances have raised the possibility of direct injury to vegetative surfaces, most work on the effects of acid rain has focused on the biogeochemical aspects of pollutants. Hypotheses have evoked both element deficiencies and toxicities. Cronan et al. (1978) and Cronan (1980), for example, comparing highly impacted and lightly impacted regions of the United States with respect to sulphate (SO_4^{2-}) loading, concluded that anthropogenic SO_4^{2-} had become (presumably within historic time) the dominant leaching anion of a high-elevation New Hampshire balsam fir (*Abies balsamea* [L.] Mill.) forest floor. With regard to element excesses, at the other extreme, Ulrich et al. (1980) proposed that, as a result of SO_4^{2-} pollution of human origin, free aluminum (Al^{3+}) concentrations in a loess-derived forest soil in central Germany had risen to toxic levels.

The underlying assumptions in the many statements on the effects of acid rain on natural vegetation are that (1) the elements made less available (either through direct removal from the root environment as by accelerated leaching or, in some way, through chemical fixation) are in already limited or nearly limited supply, and (2) the rates of removal are beyond the capability of nature to accommodate. The case of toxicity, on the other hand, presupposes rates of supply sufficiently great that natural processes (e.g., leaching, chemical fixation, immobilization within the biota, etc.) are unable to compensate.

The larger project of which the present investigation is part was formulated in 1979-1980 as the Turkey Lakes Watershed Study, to bring together current and planned research in forestry, water and fisheries on the effects of acid rain on the natural ecosystems of the Precambrian Shield of central northern Ontario. The present investigation complements several other Canadian Forestry Service initiatives at this location, particularly that of Foster and Nicolson (1984) in these proceedings. We are endeavoring to elucidate the influence of atmospherically deposited acidifying substances upon the biogeochemical properties and processes and the productivity of an old-growth sugar maple (*Acer saccharum* Marsh.)-yellow birch (*Betula alleghaniensis* Britton) forest on shallow, Precambrian-derived till soil.

Biogeochemical cycles are commonly portrayed as systems of 'pools' and 'fluxes'. The present investigation is concerned with quantifying the various element pools and element fluxes associated with the litter production/decomposition cycle (water cycle elements discussed separately by Foster and Nicolson [1984]). It is proposed that, in the annual economies of S and Ca of the present stand, fluxes of these elements associated with biomass accumulation and with the litter production/decomposition cycle are large in relation to atmospheric contributions.

STUDY AREA

The overall study area, Turkey Lakes Watershed (Lat. 47°03'N; Long. 84°25'W), is located along the common boundary of Wishart and Norberg townships, Algoma District, northern Ontario, approximately 60 km north of Sault Ste. Marie. The area is within the Algoma (L.10) Section of the Great Lakes-St. Lawrence Forest Region (Rowe 1972) and the Superior Climatic Region (Chapman 1953). The average length of growing season based on a 5.5°C index is approximately 175 days, or late April through mid-October (Chapman 1953). Mean total precipitation recorded at Turkey Lakes Watershed during the period 1980 to 1982 was approx. 1300 mm per annum[1]. Further, the overall study area is within the Batchawana Site District of Site Region 4E (Lake Timagami) (Hills 1955). The soil supporting the study stand was a Humo-Ferric Podzol (Canada Soil Survey Committee 1978) developed in shallow till of mixed granitic-basaltic origin.

The study stand, which occurred at an elevation of approx. 380 m, was typical, uneven-aged 'old-growth' sugar maple, with a lesser component of yellow birch. In addition, there was scattered red maple (*Acer rubrum* L.), ironwood (*Ostrya virginiana* [Mill.] K. Koch), red oak (*Quercus rubra* L.) and white spruce (*Picea glauca* [Moench] Voss) in the overstory and understory, and balsam fir and eastern white cedar (*Thuja occidentalis* L.) confined mainly to the understory.

Mean dominant height of the main stand was 22.1 m; mean diameter at breast height (DBH) was 19.6 cm; basal area (BA) was 28.6 m^2 ha^{-1} and gross total volume was 238 m^3 ha^{-1}. Measured stump ages ranged from 40 to 152 years. (For inventory purposes, the stand was assigned an age of 120 years in 1966, i.e., 135 years in 1981.)

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[1] R. Semkin, pers. commum.

METHODS

Biomass and Macroelements

Four 0.1-ha circular permanent sample plots were established in this stand during the spring of 1980. DBH (1.3 m above the upper groundline) was recorded to the nearest 0.1 cm for all trees > 5 cm DBH. Total heights were measured by Haga Altimeter for subsamples of trees of each species.

Individual data on tree weight came from two sources, both sampled by the same procedure, both in Algoma District and both from old-growth sugar maple forest. The first set consisted of 19 sugar maple and 25 yellow birch trees, sampled in 1978 (Thomas 1978, Payandeh 1981). Briefly, trees representing a range of diameters were felled, and above-ground dry weight was estimated by a procedure similar to that described by Hegyi (1971), though adapted for hardwoods. Fresh crown and bole weights were determined in their entirety in the field, and individual components (foliage, live branch, dead branch, stemwood and skin bark) were determined by means of various fresh weight/dry weight conversion factors developed following separation and drying of subsamples at 70°C. Root weights were determined in a similar manner following excavations of root systems. The second data set consisted of 15 sugar maple and 10 yellow birch trees felled in the study stand during the summer of 1981 and weighed in the same manner.

Data sets by components, combinations of components and whole trees were plotted separately and together, the overlays between the sets being sufficiently complete that the sets were merged to produce one larger set per species. Relationships of the form:

$$Y = b_1 X^{b_2} + e$$

where Y = individual tree biomass in kg, X = DBH, and b_1 and b_2 are parameters of the model to be estimated, as advocated by Payandeh (1981), were calculated for components and whole trees for each species. These were used in conjunction with stand table data to estimate standing-crop biomass by components for each of the four 0.1-ha plots.

Samples of foliage from all parts of the crown, of live and dead branch material, of stemwood and stembark were collected from a number of trees in the study stand during August 1981. Samples were removed to the laboratory, oven-dried to constant weight in a forced-draught oven, then ground to pass a fine mesh in a laboratory knife mill.

Nitrogen analysis was by a semimicro-Kjeldahl procedure (Mader and Hoyle 1964). Following dry-ashing at 500°C in a muffle furnace, P was determined colorimetrically by a molybdophosphoric blue procedure; K was determined by flame emission spectrophotometry and Ca and Mg by atomic absorption spectrophotometry, using conversions of the same Pye Unicam SP 1900 Atomic Absorption Spectrophotometer. Sulphur was determined turbidimetrically following $Mg(NO_3)_2$-ashing (Anon. 1960).

Data were averaged to give mean foliar, live branch, dead branch, stemwood, root, etc., concentrations for each element, and these were applied to the figures for component weight per area to give N, P, K, Ca, Mg and S contents per hectare.

Litter Collection

Annual litterfall over a 3-year period was determined by monthly collections during the growing season and again at the end of the winter from 24 1-m^2 and 24 0.25-m^2 fine mesh litter trays distributed over the 1-ha study stand. Litters were oven-dried to constant weight at 70°C, then separated into (1) leaf, (2) reproductive and (3) other litters. Subsamples were ground, stored for chemical analysis, then analyzed as above. Bioelement contents per area were calculated by multiplying per-area weights by concentrations.

Forest Floor

Forest floor bulk and organic weights were determined by quantitatively excavating 80 (20 randomly distributed per 0.1-ha plot) 0.1-m^2 samples and separating them in the field into L, F and H horizons. Dry weights of bulk samples were determined following drying to constant weight at 70°C.

Organic weight was determined by applying organic weight/bulk weight conversion factors determined for a subsample of each sample by horizon by loss-on-ignition at 500°C in a muffle furnace. Other subsamples were stored for chemical analyses according to the same procedures as above. Per-area contents were calculated by multiplying per-area bulk weights by concentrations.

RESULTS

Biomass and Macroelements

Standing-crop biomass and contents of N, P, K, Ca, Mg and S in both above- and below-ground components of the study stand (all species combined) are given in Table 1. The most abundant element in the tree layer was Ca at approx. 1100 kg ha^{-1}, followed by N > K > Mg > S > P. Approximately 97% of total Ca and 93% of total Mg were associated with woody parts, in contrast with 82-87% for other elements studied. Approximately 16% of the total tree-layer N and 18% of the total tree-layer S were associated with foliage.

Table 1. Standing-crop biomass and macroelements in an old-growth sugar maple-yellow birch stand

Component	Biomass	N	P	K	Ca	Mg	S
	kg ha^{-1}						
Foliage	4 200	93	4	45	32	5	9
Branches, live	48 400	163	10	130	320	21	16
Branches, dead	2 000	7	1	2	15	1	1
Stem bark	19 500	120	5	59	476	10	7
Stem wood	135 000	130	8	84	144	28	13
Stumps and roots	35 000	52	3	30	120	8	5
Total	244 100	565	31	350	1107	73	51

Litter Collection

Mean annual total litterfall for the study stand measured over a 3-year period beginning in 1981 was approx. 3700 kg ha^{-1}. Mean distribution by months for this period is given in Figure 1.

Mean additions of N, P, K, Ca, Mg and S to the forest floor associated with the annual litterfall are given in Table 2. The most abundant element in the annual litterfall was N, followed by Ca > K > Mg > S > P.

Table 2. Additions of elements to forest floor in annual litterfall (3-year average)

Fraction	N	P	K	Ca	Mg	S
	kg ha^{-1} yr^{-1}					
Leaves	30.0	1.0	7.2	29.8	3.5	2.7
Reproductive parts	5.5	0.4	1.7	2.1	0.4	0.4
Other	4.6	0.2	0.9	5.1	0.3	0.3
Total	40.1	1.6	9.8	37.0	4.2	3.4

Forest Floor

Weight of bulk forest floor, i.e., both organic and mineral fractions of the L, F and H horizons, averaged 59 tonnes ha^{-1} over the study stand. On average, 33 tonnes ha^{-1} of this was composed of organic matter. Distributions of organic matter and N, P, K, Ca, Mg and S in each of the L, F and H horizons are given in Table 3. The most abundant element in the forest floor was N, followed by Ca > S > K > Mg > P.

Table 3. Organic matter and macroelements in forest floor of old-growth sugar maple-yellow birch stand

Horizon	Organic matter	N	P	K	Ca	Mg	S
		kg ha^{-1}					
L	5 583	124	4	8	74	4	11
F	15 412	402	13	21	123	15	37
H	12 009	400	15	25	85	30	42
Total	33 004	926	32	54	282	49	90

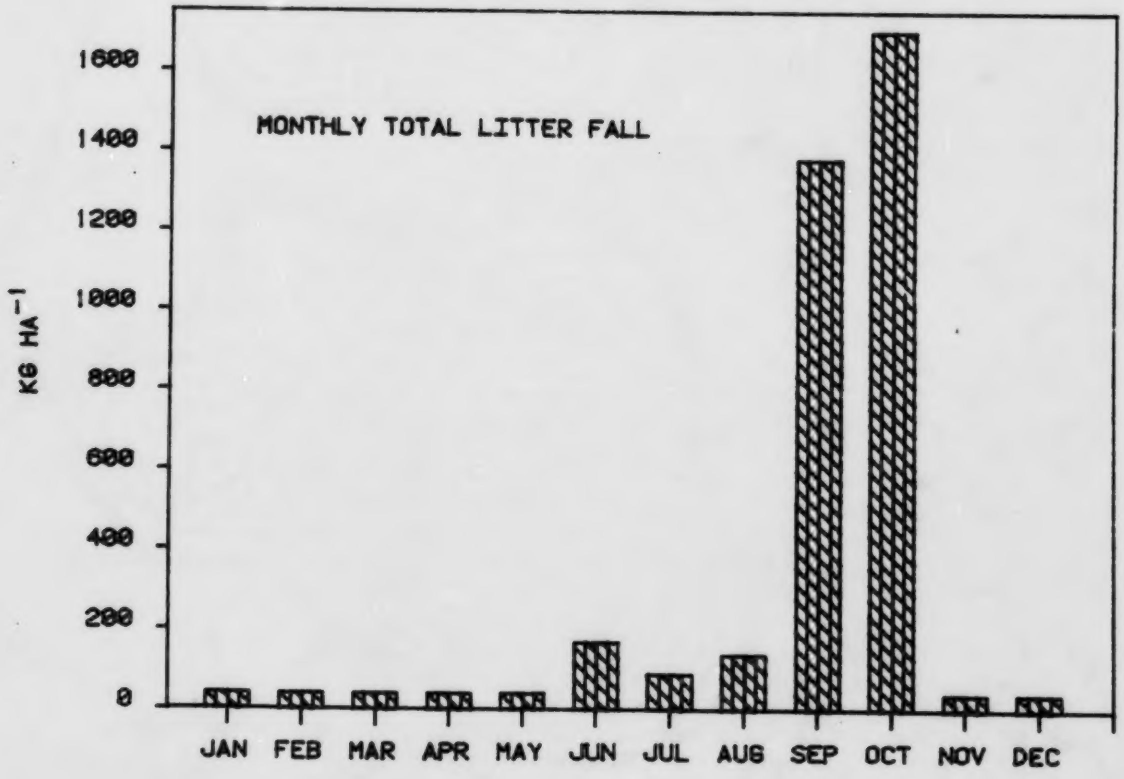

Figure 1. Monthly distribution of annual total litterfall in old-growth sugar maple-yellow birch forest (3-year average).

DISCUSSION

In comparison with other well-stocked, temperate, deciduous hardwood ecosystems on typical sites, the stand of the present study occupied an intermediate position in terms of standing biomass and bioelement stores. Total tree-layer dry-matter content above and below the ground was estimated at 244 tonnes ha^{-1}; quantities of N, P, K, Ca, Mg and S immobilized within the tree layer at age 135 years (from Table 1) were estimated at 565, 31, 350, 1107, 73 and 51 kg ha^{-1}. For a 55-year-old maple-birch-beech (*Fagus grandifolia* Ehrh.) forest at Hubbard Brook, New Hampshire, likewise on acid till soil, average standing-crop biomass was reported as approx. 165 tonnes ha^{-1} (Whittaker et al. 1974) and total tree-layer N, P, K, Ca, Mg and S contents were reported as 532, 87, 218, 484, 49 and 59 kg ha^{-1}, respectively (Likens et al. 1977). For an uneven-aged oak-hickory (*Quercus-Carya* spp.) forest on a highly weathered soil at Walker Branch, Tennessee, with an average standing biomass of 156 tonnes ha^{-1}, N, K and Ca contents were given as 470, 340 and 980 kg ha^{-1} (Henderson et al. 1978) and, at the same location, total S within the tree layer was separately reported as 72.8 kg ha^{-1} (Shriner and Henderson 1978, Johnson et al. 1982). For a 120- to 125-year-old beech (*Fagus sylvatica* L.) forest on a loess-derived soil, Solling District, West Germany, standing biomass was given as 311.4 tonnes ha^{-1} and total S-content as 68.1 kg ha^{-1} (Meiwes and Khanna 1981).

The total 51 kg ha^{-1} of S within the biomass of the present stand is not markedly less than that reported in a younger though otherwise comparable maple-birch-beech forest in more highly SO_4^{2-}-impacted New Hampshire, or in other deciduous hardwood ecosystems including highly impacted beechwoods in Solling, West Germany, or oak-hickory forest in Tennessee. In none of these stands did the biomass, in relation to other repositories for S, contain more than moderate concentrations of this element. Mean annual accumulation of S in tree biomass for the present stand is estimated at approx. 0.4 kg ha^{-1} yr^{-1}. Further, the flux of S in the annual litter production/decomposition cycle was small (approx. 3.4 kg ha^{-1} yr^{-1}) in relation to meteoric fluxes (*cf.* Foster and Nicolson 1984). Relative to other elements, S was retained somewhat in the forest floor.

On the other hand, Ca is retained within the biomass of this tolerant hardwood ecosystem in large amounts, with a sizeable pool resident within the bark of the sugar maple trees alone. The percentage of Ca in sugar maple bark was substantially higher than that in yellow birch bark (not shown) which, together with maple dominance within the stand, gave a figure of 1107 kg Ca ha^{-1}. Species differences in Ca accumulation were well demonstrated by Alban et al. (1978), who reported Ca accumulation in a trembling aspen (*Populus tremuloides* Michx.)- largetooth aspen (*P. grandidentata* Michx.) stand as 1074 kg ha^{-1}, whereas in an adjacent jack pine (*Pinus banksiana* Lamb.) stand on the same soil type, the equivalent figure was 241 kg ha^{-1}.

In the annual Ca economy of the present stand, the flux of Ca associated with the litter production/decomposition cycle was large in comparison with atmospheric inputs. Total litterfall contribution of Ca is estimated at 37.0 kg ha^{-1} yr^{-1} or 1.85 keq ha^{-1} yr^{-1}). In contrast, Foster and Nicolson (1984) estimated the 1981 H-ion input to the forest floor of the study stand through throughfall and stemflow combined at 0.27 keq ha^{-1}.

To account for Ca accumulation in the biomass, for annual losses from the tree layer in the form of litterfall, rootslough, and precipitation enrichment, total Ca uptake (i.e., 'demand') was estimated at 60 kg ha^{-1} yr^{-1} by using the equation ($U = A - P + T + S + L + R$) where U, A, P, T, S, L and R equal gross uptake, annual accumulation into the biomass and annual fluxes in precipitation, throughfall, stemflow, litterfall and root slough, respectively. If we suppose that the availability of Ca in the forest floor equalled that released by the decomposition of the previous year's litter (i.e., 37.0 kg ha^{-1}) less that incorporated into the buildup of forest floor (here, estimated at 282/135 = 2.1 kg ha^{-1}) plus that received annually as throughfall and stemflow (7.1 kg ha^{-1} from Foster and Nicolson [1984]), the resultant figure is 42.0 kg ha^{-1} yr^{-1}, which leaves 18.0 kg ha^{-1} yr^{-1} to be satisfied by Ca from deeper in the soil profile. The degree to which this represents exchangeable Ca as opposed to Ca from weathering cannot be ascertained at this time. In a separate study (Morrison 1984), however, dealing with a soil very much lower in Ca, evidence is presented that suggests enhanced weathering of Ca minerals in response to inputs of artificial acid rain.

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Effects of Artificial Acid Rain on Percolate Chemistry of Two Jack Pine Forest Soils

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ABSTRACT

Two soils, both acid glacio-fluvial sands from beneath semimature jack pine (*Pinus banksiana* Lamb.) forest in northern Ontario, Canada, were reconstructed in 1-m-deep column-lysimeters in a greenhouse compartment. Over a 5 1/2-year period, the soils, a Humo-Ferric Podzol from Wells Township and a Dystric Brunisol from Dupuis Township, were subjected on a weekly basis to artificial acid rain consisting of H_2SO_4 at pH 2, 3 and 4, together with a distilled water control (pH 5.7). The application rate of the 'rain' was equivalent to 1000 mm per year. Percolates were recovered and volumes were recorded weekly; every fourth week, pH, conductivity and concentrations of SO_4^{2-}, K^+, Na^+, Ca^{2+}, Mg^{2+} and several trace metals including Al, Mn and Zn were determined. The focus was on soil reactions as interpreted from percolate chemistry. Particular attention was paid to the course of events over time.

The results of the experiment suggest a stage-by-stage process of element loss: first, both soils, but particularly the Humo-Ferric Podzol, exhibited considerable initial resistance to base leaching, with SO_4^{2-} movement hampered by strong SO_4^{2-} retention; second, when SO_4^{2-} adsorption capacity reached the saturation point, bases moved freely with excess SO_4^{2-} ions; third, as exchangeable cations were depleted, H^+ ions increasingly dominated the charge composition; concurrently, with the pH of the percolating solutions declining from 6.5 to less than 4.0 during this stage in soils treated with acid rain having a pH of 2, there was substantial mobilization of trace metals, particularly Al.

INTRODUCTION

On two earlier occasions, results from this experimental setup were reported: first, results concerned chiefly with percolate composition and emphasizing base leaching were described to the end of three years following the beginning of treatment (Morrison 1981); second, results concerned chiefly with base leaching were described to the end of 4 1/2 years (Morrison 1983). In the present paper, results are described to the end of 5 1/2 years, with emphasis being placed on aluminum (Al) mobilization.

To test an initial hypothesis that acid rain accelerates leaching of soil bases, profiles of two low-base acid sands were restructured in column-lysimeters and subjected to a range of dilute sulphuric acid (H_2SO_4) treatments over an extended period, with percolates from all lysimeters being analyzed on a regular basis. The results portrayed a stage-by-stage process of element loss. First, both soils exhibited considerable initial resistance to cation leaching, a Humo-Ferric Podzol (Canada Soil Survey Committee 1978) more so than a Dystric Brunisol. Sulphate-ion (SO_4^{2-}) movement was hampered by strong SO_4^{2-} retention. Subsequent measurements of SO_4^{2-} adsorption properties of the study soils in comparison with those of a wide range of northern Ontario Podzolic soils[1] support the hypothesis that the soils were moderately strongly SO_4^{2-} adsorbing. Second, when SO_4^{2-} adsorption capacity had reached the saturation point, bases moved freely with excess SO_4^{2-} ions. Third, as exchangeable bases were depleted, hydrogen ions (H^+) increasingly dominated the positive charge composition of the percolating solution, as indicated by the decrease in pH which, in the case of the most acidic treatment (pH 2.0), declined from ca. pH 6.5 to less than pH 4.0 at the 1-m depth; there was substantial mobilization of trace metals including manganese (Mn), zinc (Zn) and Al during this period.

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[1] Foster, N.W. 1983. Personal communication.

The last-mentioned element, i.e., Al, is currently the focus of considerable interest because of a hypothesis advanced by Ulrich et al. (1980) in Germany which has attracted much attention and attributes diebacks of several tree species throughout central Europe to Al^{3+} mobilized in soil by acid rain. According to this hypothesis, acid precipitation induces internal H^+-ion production in soil, partly by accumulation of organic matter poor in nitrogen (N) and partly by change in N nutrition. Also, H^+-ion buffering, by dissolution of polymeric hydroxy-Al compounds, results in the formation of $AlOHSO_4$, then free Al^{3+}; Al^{3+} concentrations in the soil solution eventually reach toxic levels for forest stands.

To investigate these phenomena more fully as they relate to the soils of the present study I continued the basic experiment for another year and, in addition to using the parameters described in the earlier reports (Morrison 1981, 1983), measured percolate total Al concentrations. (Total Al had been measured at irregular intervals previously.) The purpose of the present investigation, then, is to test the hypothesis that high levels of acid have the potential to mobilize soil Al to injurious levels in acid forest soils.

MATERIALS AND METHODS

Two soils, both acid glacio-fluvial sands from beneath mid-aged jack pine (*Pinus banksiana* Lamb.) stands in northern Ontario, Canada, were chosen for the experiment. One soil was an Orthic Humo-Ferric Podzol of the Wendigo series, developed in deep, gravelly-loamy sand in Wells Township (lat. 46°25'N; long. 83°23'W), which supported an approximately 40-year-old, well-stocked pinery of fire origin. The second soil was from Dupuis Township (lat. 47°38'N; long. 83°15'W), 135 km further north, and was an Orthic Dystric Brunisol, unnamed, supporting an approximately 50-year-old well-stocked pinery, likewise of fire origin. The site class (Plonski 1974) was II in both cases. Physical and chemical properties of the two soils are available elsewhere (Foster and Morrison 1976; Morrison and Foster 1977). For convenience, the soils are hereafter referred to as 'Wells' (i.e., the Podzol) and 'Dupuis' (i.e., the Brunisol).

Bulk samples by horizons for the mineral portions of the profiles (Wells: Bf, BC, C; Dupuis: Bm, IIBm, C) were collected at the two locations during the summer of 1977. The soils were allowed to air-dry, then were coarse-screened through a 7.7-mm screen to remove larger fragments. The horizons in appropriate sequence and thicknesses were reconstructed in columns of clear acrylic plastic, 1 m deep and 165.3 cm^2 in cross-sectional area. Each column was mounted on a perforated lysimeter plate, with a collecting arrangement for percolates (effluents). Thin layers of laboratory-grade glass wool and sieved, washed perlite were inserted at the base of each column to facilitate drainage. The LFH and Ae horizons in each case were excavated intact, trimmed to size and inserted in the column tops. Columns were foil-wrapped to exclude light and were set up in an isolated greenhouse compartment. The experiment consisted of two soils x four treatments x three replicates for a total of 24 columns. Before the experiment was begun, all columns were leached several times with distilled water to expedite settling.

Solutions of pH 2, pH 3 and pH 4 were prepared by appropriate dilution of H_2SO_4. Distilled water (DW) served as a fourth or 'control' treatment. Volumes were adjusted to an annual rate of 1000 mm, roughly equivalent to ambient mean total precipitation in the region. Solutions were delivered by a drip-feed system for a period of 1-2 hours every week. The columns drained freely by gravity and effluents were recovered, usually the day following application. Treatment began in October 1977 and the experiment has been running continuously since then.

Percolate volumes are recorded following each weekly application. Other parameters were measured weekly at first, but now are measured only every fourth week. These include pH by glass electrode pH meter; specific conductance by Radiometer Type CDM 2e conductivity meter; SO_4^{2-} originally by a barium chloride titrimetric method but recently colorimetrically by a methylthymol blue procedure with a Technicon Auto-Analyzer II, potassium (K), sodium (Na), calcium (Ca), magnesium (Mg) and Al by flame emission or atomic absorption as appropriate, using (1) Pye-Unicam SP1900 and more recently (2) Varian Model AA-975 and (3) Varian Model AA-1275 atomic absorption spectrophotometers. Major cations determined on a regular basis include K, Na, Ca and Mg; trace elements include Mn, Zn, iron (Fe) and Al. Where instruments or procedures changed over the course of the experiment, conversion factors were developed to ensure comparability of results.

RESULTS

As was the case previously with percolate analyses, only those of the pH-2 series differed significantly in composition from those of the control series; hence, for clarity, graphical comparisons (Figs. 1-3) are restricted to those treatments only.

During the period 4 1/2 to 5 1/2 years, SO_4^{2-} levels (Fig. 1) in percolate from the pH-2 Dupuis series continued to approximate input levels; SO_4^{2-} levels in percolate drom the pH-2 Wells series just reached input level during this period.

During the same period, total major cation (K, Ca, Mg, Na) concentration (Fig. 2) in percolates from both pH-2 series, but the Dupuis more than the Wells, continued to decline, reaching stability in the pH-2 Dupuis series, though at a level substantially higher than that of the control. The chief contributors (not shown) in terms of molar concentrations to the charge difference between the pH 2 and control treatments were Ca followed by Mg > Na > K for the Dupuis soil and Mg > Na > K > Ca for the Wells soil.

During the period 4 1/2 to 5 1/2 years, the pH of both pH 2- series percolates continued to decline (Fig. 3) and, during this same period, there were increasing concentrations of total Al in percolates from both pH-2 treated series but not others. Mean concentrations of total Al by treatment for both soils for week 256 are given in Table 1. Plotting (not shown) of several months of percolate Al on SO_4^{2-} concentrations for individual lysimeters, by treatment, revealed generally consistent relationships between Al and SO_4^{2-} concentrations in percolates under given sets of conditions.

Table 1. Concentration of total aluminum in week 256 percolates from Wells and Dupuis soils subjected to different acid treatments

Treatment	Wells	Dupuis
	µg mL^{-1}	
DW	0.02	0.01
pH 4	0.02	0.02
pH 3	0.01	0.01
pH 2	50.73	59.46

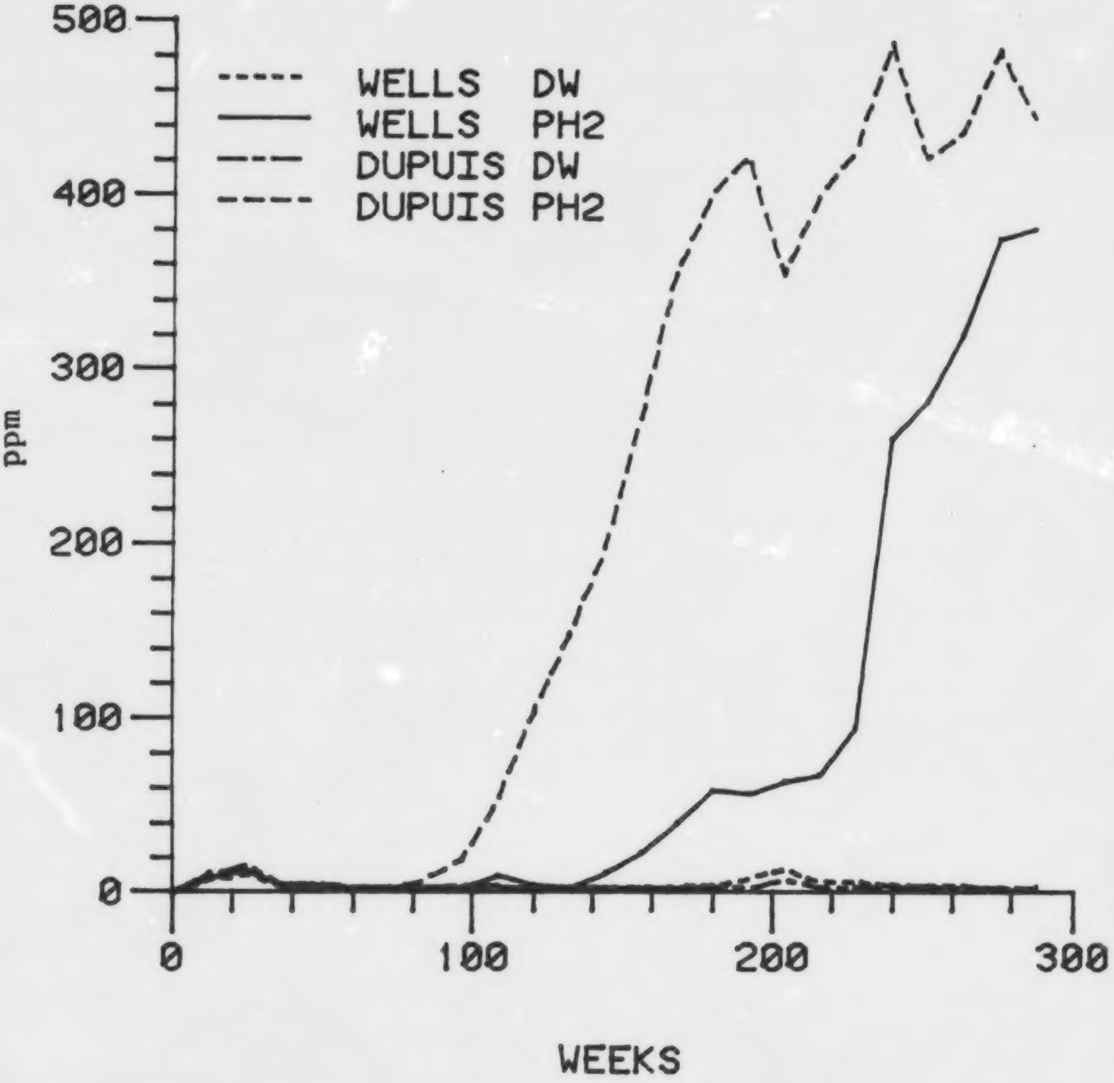

Figure 1. Change over 5 1/2 years in SO_4^{2-} concentration ($\mu g\ mL^{-1}$) in percolates from Wells and Dupuis soils subjected to different acid treatments.

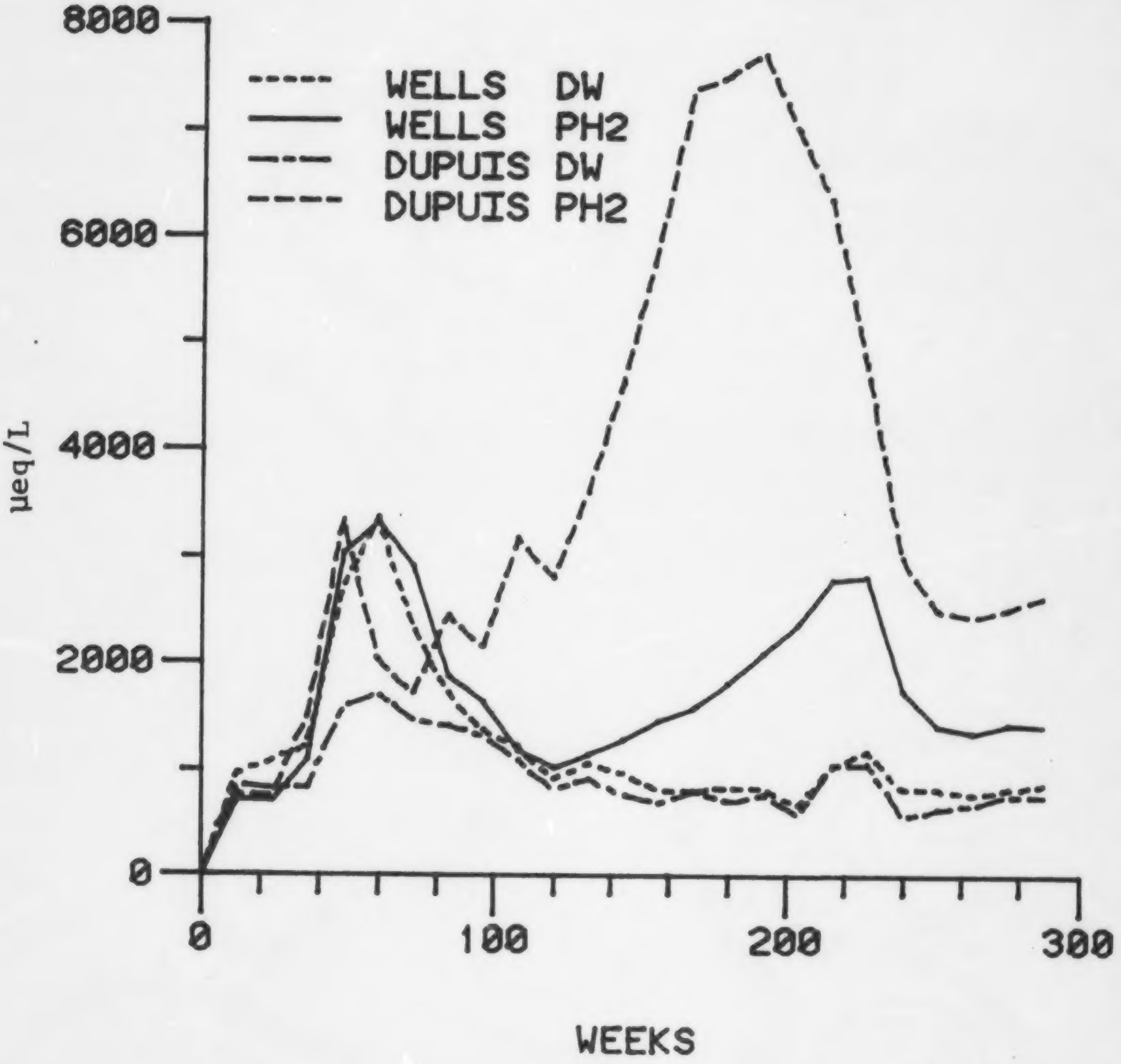

Figure 2. Change over 5 1/2 years in total major cation (K + Na + Ca + Mg) concentration (µeq mL^{-1}) in percolates from Wells and Dupuis soils subjected to different acid treatments.

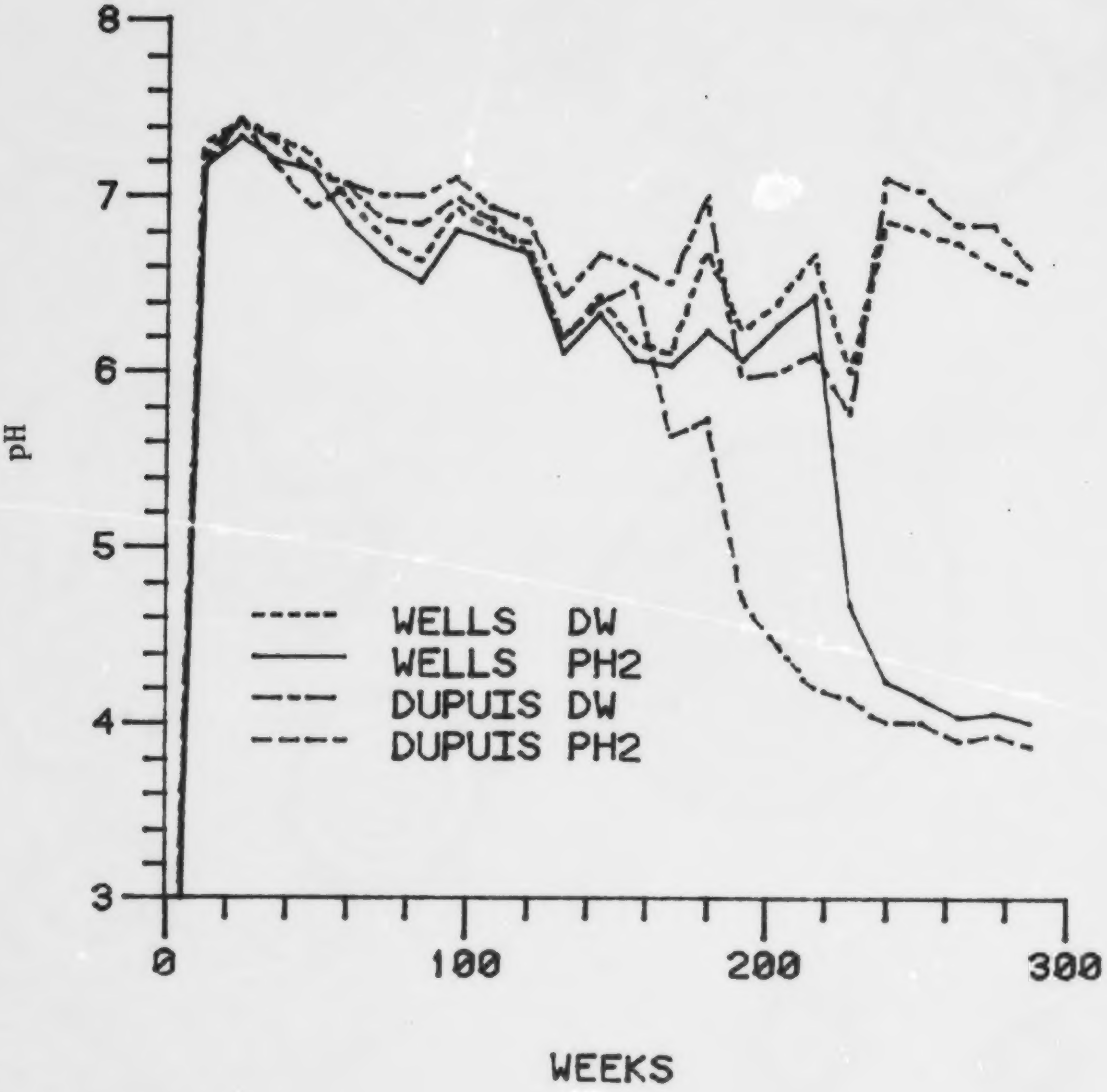

Figure 3. Change over 5 1/2 years in pH of percolates from Wells and Dupuis soils subjected to different acid treatments.

DISCUSSION

The intent of the present experiment was not to reproduce a natural system in miniature as is implicit in the term 'microcosm' applied by some authors to experiments that use similar apparatus, since in the present instance no attempt was made to account for wetting/drying cycles, freezing/thawing cycles, annual inputs of litter and the decomposition thereof, or the uptake of various elements by plants. Rather, the intent was to provide a simplified, relatively controlled system for the study of soil chemical processes. A number of comparable experiments, also concerned with acid rain, have been described in the literature. The chief features of the present experiment in comparison with many others, however, are (1) the relatively low loading rate in terms of volume, which is equivalent to an annual rainfall of 1000 mm, and (2) the duration of the experiment (nearly 6 years thus far). An experiment described by Lee and Weber (1980, 1982) on a Typic Halpumbrept soil (Soil Survey Staff 1975) most nearly corresponds to the present experiment in terms of loading rate and duration, with applications from 1310 to 1732 mm per annum and a duration of 3 1/2 years. The lysimeters in this particular study, however, were planted to sugar maple (*Acer saccharum* Marsh.) or red alder (*Alnus rubra* Bong.) seedlings and a concerted effort was made to reproduce natural processes. In contrast with this experiment, several others have been described in which greatly accelerated application rates were used. Overrein (1972) reported leaching of Ca from a Norwegian podzolic forest soil exposed to artificial acid rain of pH 3.0 applied over a 40-day period at a rate of 500 mm per month (annual rate: 6000 mm) and Singh et al. (1980), also in Norway, described the distribution of $^{35}SO_4^{2-}$-S in iron podzols and semipodzols exposed to artificial acid rain over an 18-day period (applied at an annual rate of ca. 18 000 mm). In New Hampshire, USA, Cronan (1980) described products of leaching from balsam fir (*Abies balsamea* (L.) Mill.) forest floor samples exposed over a 3 1/2-month period to artificial acid rain at an annual rate of 2555 mm. Other authors (e.g., Haman 1977) have extracted soil by using dilute acid solutions.

Results of the present experiment to the end of 4 1/2 years were reviewed briefly in the Introduction. During the period 4 1/2 to 5 1/2 years, trends continued. In particular, major cations were depleted from both soils. The pattern of depletion in the pH 2-treated soil, i.e., peak followed by decline to a new stable level, suggests rapid displacement of exchangeable forms and, at the same time, treatment-related enhanced weathering of base minerals. The continued rapid decrease in pH was associated with an increase in trace metal, particularly Al, concentrations.

It is generally accepted that, in surface soils, Al exists mainly in organic combination, and that, with increasing depth, inorganic forms predominate. Frink and Peech (1962), Dalal (1975), Marion et al. (1976) and others have emphasized the central role of gibbsite, $Al(OH)_3^0$, in regulating Al solubility in many (particularly low-Al) soils. Reviewing the literature, Nair and Prenzel (1978) note that, while in earlier investigations Al species over the range of pH were perceived primarily to form a stepwise series of monomeric hydroxides, it is now generally recognized that a large number of both mononuclear and polynuclear species exist. On the basis of equilibrium calculations, however, Nair and Prenzel (1978) predicted that, all other conditions being equal, the relative amounts of Al species existing at a given pH are dependent on total Al concentrations, and that the polynuclear ions $Al_7(OH)_{17}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$ are important. On the other hand, $Al(OH)_3$ acted in a predominant fashion only in dilute Al solutions.

Van Breemen (1973), on the other hand, studying strongly SO_4^{2-}-affected acid mine soils, predicted a reaction of H_2SO_4 with various hydroxy-Al compounds and the formation of a basic aluminum sulphate of the form $AlOHSO_4$, which compound, in turn, regulates the upper limit of dissolved Al in such soils. Others have extended this possibility to soils influenced by H_2SO_4-bearing acid rain. Ulrich et al. (1980) proposed that two-thirds of the buffering of H^+ ions in a loess-derived forest soil in central Germany was by dissolution of polymeric hydroxy-Al compounds with the formation of $AlOHSO_4$ and eventual release of Al^{3+} ions to toxic levels.

In the present experiment, Al was determined as total Al, species not being separated. Under the experimental conditions, total Al concentrations produced in response to the strongest treatment (pH-2) were substantially higher (ca 50-60 μg mL^{-1}) than 'high' concentrations (ca. 2-4 μg mL^{-1}) reported in nature (e.g., Cronan et al. 1978; Ulrich et al. 1980; Budd et al. 1981; Mollitor and Raynal 1982). Models explaining the present result must conform to conditions for high SO_4^{2-} throughput, variable but decreasing pH, and high total Al concentrations. The first hypothesis, that Al ions are essentially displaced from adsorption sites by H^+ and other ions, fails to satisfy on several grounds: i.e., despite early SO_4^{2-} fluxes through both Dupuis and Wells pH 2-treated soils and despite some SO_4^{2-} flux at present in at least the Dupuis-pH-3 series, there was little indication of Al mobilization without lowering of pH. Further, the quantities involved (Al contributes ca. 75% of the total positive charge in pH-2 series leachates) suggest mobilization of hitherto insolute Al. Second and third hypotheses, viz. that the H^+ ion surplus drives the dehydrolysis of mineral hydroxy-Al towards more soluble forms which, in turn, are leached in association with excess SO_4^{2-}, or that H_2SO_4 by itself reacts with hydroxy-Al compounds to yield Al-sulphates, which in turn regulate the availability of free Al^{3+}, are generally consistent with most observations. The one observation, however, that reactions do not begin until H^+-ions in percolates are abundant, favors the hypothesis that in these two soils reactions are driven by the H^+ ion alone, with SO_4^{2-} acting primarily as leaching counter ions.

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Ion Movement in Terrestrial Basins in the Turkey Lakes Forest Watershed

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ABSTRACT

Twenty small feeder streams with basins of 4-65 ha are being monitored in the Turkey Lakes Forest Watershed (1100 ha) so that their contribution to the main aquatic system can be estimated and gross chemical changes in the terrestrial ecosystem measured. Unit flow rates, in five streams selected for presentation in this paper, ranged from 5.0 to 6.3 m^3 ha^{-1} yr^{-1} with snowmelt providing 38 to 55% of total annual discharge. Streams draining headwater areas with shallow soil are generally lower in pH, alkalinity, and conductivity than streams in the main watershed in areas with deeper soil at lower elevations. Feeders with large groundwater flow, as evidenced by annual temperature profiles, have the highest alkalinities and higher values for some major ions, primarily because percolating water has more contact time with soils and unweathered parent material. Nitrogen (N) input exceeded outputs in four of five watersheds; therefore, N appears to be accumulating in this ecosystem. Output of major cations–calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+)–exceeded input by precipitation in all cases except for K^+ in one watershed. Sulphate-sulphur (SO_4^{2-}-S) input and output are nearly in balance in four basins. Bicarbonate, as reflected in alkalinity values, was more important in balancing cation losses in areas of lower elevation and deeper soil, whereas sulphate appears to play this role in shallow-soil headwater basins. Chemical variability between streams in a watershed can be large and some areas are sensitive to increased hydrogen (H^+) ion load.

INTRODUCTION

In 1979 a small (1100 ha) watershed was selected from 100 candidates to become the focal point of a multidisciplinary, multiagency research project. The Turkey Lakes Forest Watershed (TLFW), Algoma District, Ontario, is one of three calibrated watersheds established by the Department of the Environment for the study of the long-range transport of air pollutants (LRTAP) in Canada. Cooperating in the TLFW study are representatives from Great Lakes Fisheries Research Branch (GLFRB) of the Department of Fisheries and Oceans (DFO), Atmospheric Environment Service (AES), National Water Research Institute (NWRI) and National Hydrology Research Institute (NHRI) of the Environmental Conservation Service (ECS), Ontario Ministry of Natural Resources (OMNR), and Great Lakes Forest Research Centre (GLFRC) of the Canadian Forestry Service (CFS). These agencies, along with other cooperators and contractors, are studying most aspects of the air-land-water interactions of acid rain from two points of view: the effects of acid rain on the systems, and the modification of acid rain by the system. GLFRC is studying the terrestrial aspect of the watershed: forest soils, tree biology, and forest hydrology.

The TLFW contains a chain of four lakes, the last one in the system being Turkey Lake, which discharges into the Batchawana River and then into Lake Superior. Lying approximately 60 km north of Sault Ste. Marie, Ontario, the watershed is on the Canadian Shield in an area considered to have sensitive geology and a moderate loading of atmospheric acids.

The lowest elevation in the watershed is 244 m, about 60 m above Lake Superior, and the highest elevation is Batchawana Mountain on the northern boundary at 644 m. Surficial materials in which the mainly podzolic soils have developed are largely bouldery ablation tills, variable in depth, generally shallow on crests and upper slopes and increasing in depth downslope. Bedrock is mainly greenstone with two small areas of granite: one near Little Turkey Lake and the other northeast of Batchawana Lake, which is the headwater lake of the system. Vegetation can generally be characterized as old-growth (120-180 years) sugar maple (*Acer saccharum* Marsh.) - yellow birch (*Betula alleghaniensis* Britton) forest (86% sugar maple and 3.4% yellow birch working groups, respectively).

CFS efforts are directed mainly at following the biogeochemical cycle from precipitation through the vegetative canopy and the soil system and then to the feeder streams which drain the small basins within the main watershed. The quality and quantity of the water in these small feeder streams will be discussed in this paper. These streams, along with water percolating to the groundwater system, are a major end product of the terrestrial part of the hydrologic cycle. On the other hand, the chemistry and flow of these feeder streams, along with groundwater and precipitation, are a major input to the lakes and interconnecting streams of the main aquatic system. Therefore, the parameters measured on the small feeder streams serve a twofold purpose: first, as a final output of the terrestrial system, and second, as an input to the main aquatic system.

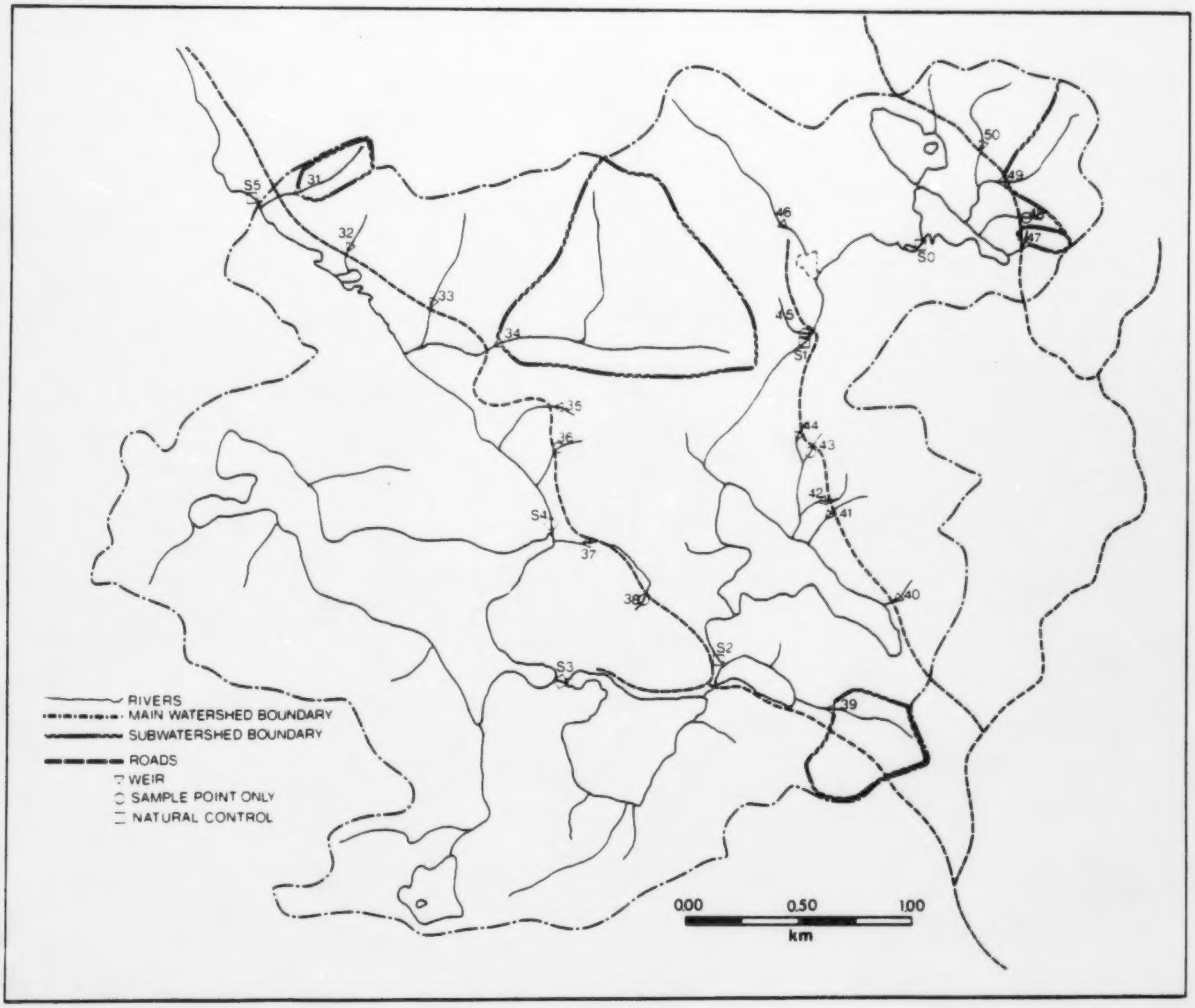
MATERIALS AND METHODS

Within the TLFW, 20 small basins of 4-65 ha are being sampled (Figure 1, streams 31 to 50). Streams 31 to 39 lie at lower elevations in the watershed and tend to have the deepest soils. Streams 40 to 46 are at intermediate elevations, and streams 47 to 50 are in the headwater area where soils are thin.

Fourteen of the streams have had plywood or concrete walls with either 90- or 120-degree V-notch blades installed to create a pool and control flow. Water levels, in stilling wells made from metal culvert pipe, were recorded by Leupold-Stevens A-71 automatic water level recorders. With these devices and periodic manual measurements of flow rates we can establish a relationship wherein the water level in the pool is all that is needed for continuous accurate measures of discharge from these small watersheds. Natural controls were not acceptable because errors involved in measuring small streams would have been too great. As for the six remaining streams, either they were small intermittents or else it was impracticable to install a control wall. These are monitored by periodic manual gauging to obtain a measure of their runoff contribution. Because of the large number of small terrestrial basins, there are opportunities not only for monitoring natural chemical variability over the area, but also for investigating reasons for the chemical differences and defining different reactions to, and upon, acid precipitation.

For this paper, five streams were selected so that a preliminary indication of chemistry and flow conditions in the feeder streams could be provided. Stream 31 drains a 7-ha basin with moderately steep slopes, some rock outcrops, and a ponded depression at the top. Stream 34 drains 63 ha, flows year-round, and has long, gentle slopes that allow percolating water more contact time with fairly deep soils. Stream 39 has a 17-ha basin and relatively deep soils, and the annual temperature profile indicates a major groundwater component in the discharge. Stream 47 with a 4-ha basin has very shallow soils and prevalent granitic bedrock. Stream 49 drains 19 ha, has some soil and flat areas, but contact time of percolating water still appears brief. Streams 31, 34, and 39 are at the lowest elevations in the main watershed whereas streams 47 and 49 are at the highest elevations in the headwater lake region.

Stream water samples were collected on a weekly basis through the open water season, approximately April to December, and every second week on six heated weirs and others remaining open naturally through the winter period, December through March. Also, intensive sampling was done on a daily basis, if possible, during spring runoff.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47
48
49
50
RIVERS
MAIN WATERSHED BOUNDARY
SUBWATERSHED BOUNDARY
ROADS
WEIR
SAMPLE POINT ONLY
NATURAL CONTROL
0.00
0.50
1.00
km

Figure 1. Turkey Lakes Forest Watershed drainage pattern

Rainfall was collected after every rain 'event' at a specially constructed platform in a beaver meadow near the main outlet. During the winter, fresh snow samples were collected every two weeks on snow boards set on the snowpack. These precipitation measurements, along with the stream measurements, are used in input and output estimates needed for assembling water and nutrient budgets for each small basin; these budgets are then related to overall budgets for the main watershed.

Chemical analyses with the following equipment and related techniques were conducted on the samples at GLFRC. Alkalinity was determined on a Metrohm 636 Titroprocessor, pH on a Fisher-Accumet 750 selective ion electrode, and conductivity on a Radiometer meter. Nitrogen (N) and phosphorus (P) forms, as well as sulphate-sulphur (SO_4^{2-}-S), silicon dioxide (SiO_2), and chloride (Cl^-) were analyzed on a Technicon Autoanalyzer Moder II-C+. Other major ion [calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+)] contents were determined on a Varian 1275 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Water production from the five watersheds was similar, based on unit flow rates that ranged from 5.0 to 6.3 $m^3 ha^{-1} yr^{-1}$ (Table 1). The period of snowmelt is the most important time of year for water production: in 1981, 38 to 55% of the annual flow occurred in the approximately six-week period of spring runoff. Volume-weighted averages indicate that headwater streams (47, 49) are more acid, as is shown by pH values 1 to 1.5 units lower than those for the other three streams; electrical conductance values are about two-thirds those of the other streams; and alkalinity values are about 14 times lower than those of the other streams–all of which indicates a reduced buffering capacity (Table 1). The alkalinity values reflect the importance of the bicarbonate ion in balancing cation losses in streams 31, 34, and 39, but they contribute very little in the headwater streams (47, 49). These observations mainly reflect the fact that the lower-elevation streams (31, 34, 39) have deeper soils and therefore more contact time so that the soil can modify the incoming precipitation. Runoff conditions during springmelt may not allow for this extended contact time; however, separate consideration of this important period will have to wait for treatment in a future paper.

Table 1. Flow parameters and other annual averages for 1981 (volume weighted)

Stream	Unit flow ($m^3 ha^{-1} yr^{-1}$)	% of flow in spring runoff	pH	Conductivity ($\mu S/L^{-1}$)	Alkalinity ($\mu eq/L^{-1}$)
31	5.02	51	6.70	43	152
34	6.32	41	6.59	38	93
39	5.51	55	6.87	53	246
47	6.17	44	5.15	30	3
49	5.83	38	5.96	29	20

Feeder streams that have a major portion of their discharge contributed by groundwater, as is evidenced by their annual temperature profiles (stream 39), have the highest alkalinities and higher values of some major ions, primarily because percolating water has more contact time with soils and unweathered parent material.

Nitrate-nitrogen (NO_3^--N) output is less than precipitation input in four of the five watersheds (Table 2). Forests that receive large atmospheric deposition of NO_3^--N do not necessarily have large outputs; for example, at Coweeta Hydrologic Laboratory, North Carolina, USA, input was 6.39 kg ha^{-1} yr^{-1} and output 0.16 (Swank and Douglas 1977). At Walker Branch, Tennessee, USA, input was 13.0 and output 3.1 (Henderson and Harris 1975). At Hubbard Brook, New Hampshire, USA, it was reported that NO_3^--N losses were low during the growing season; however, after cessation of vegetative uptake in the autumn, stream discharge of NO_3^--N markedly increased (Likens et al. 1977). Nitrate losses are strongly regulated by both microbial transformations and vegetation uptake rather than by levels of atmospheric inputs.

Table 2. Annual cycling (kg ha^{-1} yr^{-1}) of nitrogen for 1981

			NO_3^--N	NH_4^+-N	Organic N	Σ N
Input						
	Precipitation		6.10	3.22	2.43	11.75
Output						
	Stream	31	5.24	0.081	1.74	7.06
		34	4.66	0.102	2.22	6.98
		39	4.53	0.091	1.99	6.61
		47	9.26	1.048	6.09	16.40
		49	4.17	0.107	1.99	6.27

Ammonium-nitrogen (NH_4^+-N) output is lower than input in all five watersheds, organic-N output approaches input values in four watersheds and exceeds the input value in the fifth watershed, and total N output exceeds input in only one watershed. Further investigation of watershed 47 may be necessary to explain the elevated amounts of all forms of N. This may simply be a problem with definition of watershed size in an area of jumbled surface configuration and steep slopes. Unit discharge and elemental concentration values are similar to those of the other four watersheds. Surface area is the only other variable in the calculations.

As precipitation inputs of N exceeded streamflow outputs in most cases, N appears to be accumulating in this ecosystem. A tight cycle of N was maintained in this undisturbed ecosystem and the internal cycle of N was considerably larger than the amounts of N discharged from the watershed in streamflow (Foster et al. 1983).

Output of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) in streamflow exceeded the input by precipitation in all watersheds except in the case of K^+ in stream 49 (Table 3). This indicates a net loss of these ions from the ecosystem. The origin of the cations is uncertain. Elements leaching from the rooting zone ultimately end up in streamflow. Streamflow, however, also includes elements leached from unsaturated and saturated soil below the rooting zone and bedrock in contact with groundwater.

Hydrogen-ion (H^+) output in streamflow was substantially lower than the input by precipitation (Table 3). Therefore, H^+ is accumulating in the ecosystem, or conversely, a decrease in acidity has occurred through contact of precipitation with the vegetation and soil components of the watershed.

Table 3. Annual cycling (kg ha^{-1} yr^{-1}) of ions for 1981

		Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	SO_4^{2-}-S
Input							
Precipitation		5.43	1.10	1.75	2.12	0.59	10.21
Output							
Stream	31	26.94	3.14	2.48	3.85	0.0010	11.89
	34	29.92	3.61	2.29	4.31	0.0016	14.99
	39	42.78	3.59	1.99	3.26	0.0007	13.92
	47	34.55	5.49	2.26	5.74	0.0614	31.09
	49	17.75	2.90	1.48	3.05	0.0064	12.29

Output of SO_4^{2-}-S) is nearly in balance with input in four of the basins. Stream 47, however, once again differs from the others because of a SO_4^{2-}-S output over three times larger than precipitation input. Increased SO_4^{2-}-S output in stream 47 resulted in greatly increased cation output. A reduction in the quantity of SO_4^{2-}S entering the forest ecosystem would likely result in reduced cation losses from the headwater basins and, to a lesser extent, losses from the basins at lower elevations.

Chemical variability between terrestrial feeder streams within a watershed can be large and some areas may be sensitive to an increase in acidity. Data collection is progressing and future investigations will add to the knowledge accumulating on this important forest ecosystem.

ACKNOWLEDGEMENTS

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The Interaction Between Mobile Anions and Aluminum in a Shallow Podzol

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INTRODUCTION

The chemical properties of aluminum play a significant role in the acidification of soils and freshwaters. Several compounds and dissolved complexes act as proton buffers (e.g., Ulrich et al. 1979). High aluminum concentrations can also cause toxic effects in streams and lakes, which have a low level of other dissolved electrolytes (Baker and Schofield 1980; Muniz and Leivestad 1980). It has even been claimed that such effects might occur in naturally acid soils, although the organisms inhabiting such soils should be adapted to the acidic conditions (Ulrich et al. 1979; Ulrich 1983; but see Abrahamsen 1983). The release and transport mechanisms of aluminum are obviously of great interest, both for an accurate understanding of the reasons for the high aluminum concentrations found in many acid freshwaters and for research concerning the possible effects on soil biota.

In this paper, data are presented which illustrate the importance of different anions for the aluminum concentration found in the soil solution of a shallow podzol under mixed coniferous forest on the Swedish west coast. The site is situated within the L. Gårdsjön catchment (58°04'N, 12°03'E). The catchment has been intensively studied since 1979 within the framework of an integrated research project, which addresses the problem of soil and lake acidification from both the biogeochemical and biological point of view (Andersson and Olsson 1983).

SITE DESCRIPTION

The drainage area of L. Gårdsjön is 74.3 ha and the lake itself has an area of 31.2 ha. The morainic soil has a clay content varying between 4% and 11% (Melkerud 1983). It is characterized as an iron humus podzol or an iron podzol, the profile type depending on the topographical location and the concomitant water regime. The average soil depth is only 50 cm, and a typical C horizon is often lacking. This means that the lower B horizon is in immediate contact with the bedrock, which is dominated by granites and gneisses with some inclusion of granodiorite.

The tree vegetation is dominated by Norway spruce (*Picea abies*). Other tree species are Scots pine (*Pinus silvestris*) and birch (*Betula verrucosa*). The current annual deposition of sulphur and nitrogen (wet plus dry) is 24.8-31.1 kg ha^{-1} and 16.2-22.6 kg ha^{-1} respectively (Grennfelt et al. 1983). Mean pH in the lake is 4.7 and the mean aluminum concentration is 11 μM (Hultberg 1983; Nilsson 1983).

FIELD AND LABORATORY METHODS

The soil solution data were obtained from chemical analysis of lysimeter leachates. The lysimeters consisted of intact soil cores of varying length (5, 15, 35, and 55 cm) confined in plexiglass cylinders. The forest floor was included, but no vascular plants. Besides aluminum, several other dissolved components were studied, among them some heavy metals and organic carbon. Aluminum was partitioned into organic and inorganic species by using the ion exchanger technique developed by Driscoll (1980 a, b). For further details concerning field and laboratory methods, see Nilsson and Bergkvist (1983).

RESULTS AND DISCUSSION

It was recently shown by Nilsson and Bergkvist (1983) that aluminum mobility in the soil is regulated by two distinctly different processes:

- Formation of dissolved organic species in the A horizon (soil depths 5 cm and 15 cm). These organic complexes are to a large extent precipitated in the upper part of the B horizon (soil depth 35 cm). Highly significant correlations are found between the concentration of organic aluminum species and that of dissolved organic carbon at each of the four soil depths.

- Formation of dissolved inorganic species, which increase in importance with increasing soil depth. There are strong indications that basic aluminum sulphates buffer the aluminum concentration in the lower part of the B horizon (soil depth 55 cm), which also seems to be the case in superficial groundwater aquifers (Lee 1983).

The previous paper about the lysimeter study was based on data collected during the period July 1980 - September 1981, when no nitrate analyses were performed. These analyses started in 1982.

Here I specifically discuss the importance of nitrate production and nitrate transport for aluminum mobility.

Table 1 gives some basic information concerning the average concentrations of some of the dissolved components. The depth distribution of the different aluminum forms and that of nitrate are especially noteworthy. On a number of sampling occasions, the nitrate concentration in leachates from the lower part of the B horizon became very high. As the nitrate peaks were largely confined to this part of the soil, they seemed to result from nitrification rather than from any direct influence of the atmospheric deposition of nitrogen. There was a positive correlation between the concentration of nitrate and inorganic aluminum species, as illustrated in Figure 1. This figure also shows the negative correlation between inorganic aluminum and sulphate at the same soil depth. It has been repeatedly claimed that one of the main effects of "acid rain" is an increased leaching of cations, including inorganic aluminum hydroxy complexes, due to an increased flux of mobile anions among which sulphate plays a key role (e.g., Seip 1980). The graphs in Figure 1 might therefore look puzzling at first sight. They become understandable if a basic aluminum sulphate is one of several aluminum sources and if protons formed in the nitrification process release additional amounts of aluminum from, for example, gibbsite or secondary minerals such as kaolinite.

Table 1. pH and the concentration of organic aluminum complexes (Al_o), inorganic aluminum complexes (Al_i), sulphate, and nitrate. Mean values ±SD for 1982.

Soil depth		Al_o	Al_i	SO_4^{2-}	NO_3^-
cm	pH		µM		
5	4.2 ± 0.2	5 ± 3	1 ± 1	277 ± 142	89 ± 74
15	4.2 ± 0.2	30 ± 19	13 ± 16	177 ± 75	52 ± 32
35	4.2 ± 0.2	20 ± 12	49 ± 23	202 ± 55	23 ± 24
55	4.6 ± 0.3	12 ± 6	112 ± 59	259 ± 84	243 ± 293

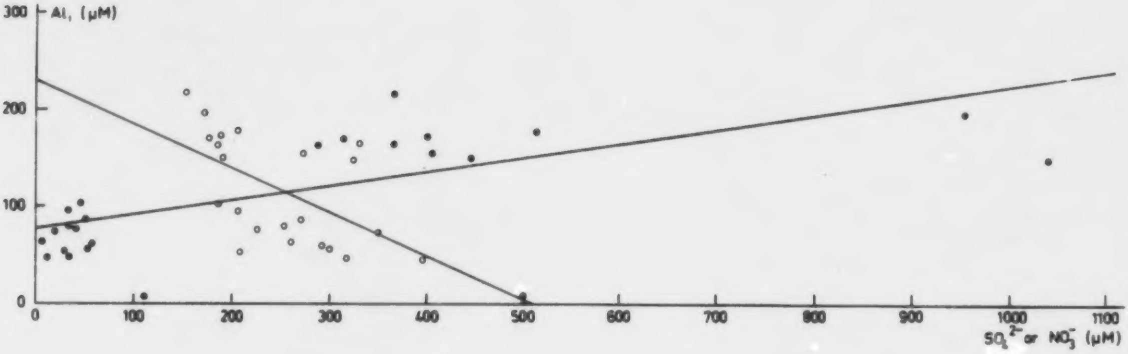

Figure 1. Linear plots of the sulphate concentration against the concentration of inorganic aluminum species (Al_i), open circles, and of the nitrate concentration against the concentration of inorganic aluminum species, closed circles. The data are obtained from lysimeter leachates collected from the lower part of the B horizon (soil depth 55 cm).

$C_{Al_i} = 228.68 - 0.45CSO_4^{2-}$ $R^2 = 0.42$ $p < 0.001$
$C_{Al_i} = 75.58 + 0.15C_{NO_3^-}$ $R^2 = 0.54$ $p < 0.001$
C_{Al_i} etc. stands for the concentration expressed as μM.

The activities of trivalent aluminum and sulphate were estimated as described by Nilsson and Bergkvist (1983), and the sulphuric acid potential ($pH + 1/2pSO_4$) was plotted against the aluminum potential ($pH - 1/3pAl$), as shown in Figure 2. This figure also shows the equilibrium lines for a number of compounds, their stoichiometric formulae and reported pK_s values. The general impression obtained from Figure 2 is that practically all data points are within the stability fields of the four basic aluminum sulphates. Also, gibbsite is of minor importance for the buffering of the aluminum concentration, which does not exclude the possibility that it could be one of the other aluminum sources.

CONCLUSION

This study indicates that a high nitrification potential in an acid soil has implications for the aluminum concentration in the soil solution. It should be emphasized, however, that the data presented here must be treated with caution, as the ion fluxes in the lysimeters are not influenced by root uptake. The experimental situation thus resembles, to some extent, the situation obtained after a clearfelling. The results give rise to some interesting speculations about the future, however. There is, at present, a steady increase of the atmospheric deposition of nitrogen, primarily with respect to nitrate, in many parts of both Europe and North America (e.g., Likens et al. 1980; Rodhe 1982), whereas the sulphur deposition seems to remain constant or even decrease.

Therefore, it is not unreasonable to envisage a future situation when the nitrate output from certain forest ecosystems will be substantially larger than today. The ecosystems in question would be those that already have a high availability of soil nitrogen and a high nitrification potential. It is to be expected that the increase in nitrate output will be most pronounced after a clearfelling (Wiklander 1981; Vitousek 1981; Vitousek et al. 1982). In acid soils with easily mobilizable aluminum compounds such as basic aluminum sulphates, there could also be an increased aluminum release.

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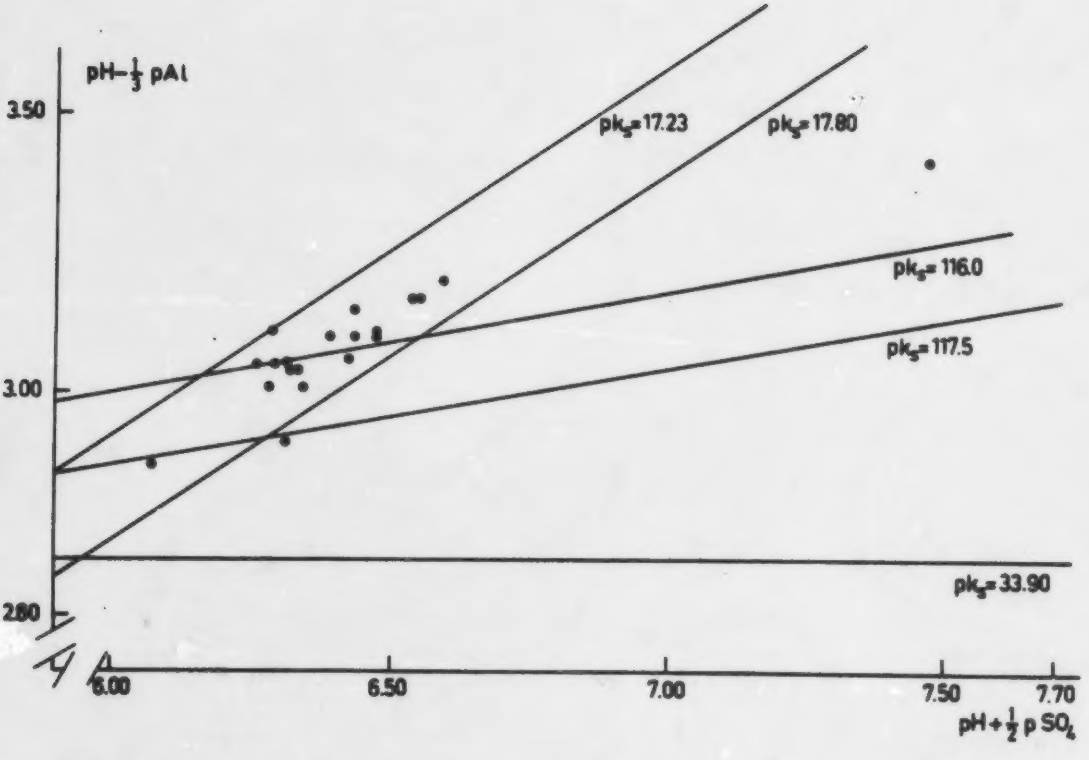

Figure 2. The sulphuric acid potential, pH + 1/2pSO$_4$, plotted against the aluminum potential, pH - 1/3pAl. The calculations are based on data from the same B horizon leachates as in Figure 1. Also shown are a number of equilibrium lines and reported pK$_s$ values:

Gibbsite, Al(OH)$_3$, pK$_s$ = 33.90 (May et al. 1979)
Basaluminite, Al$_4$(OH)$_{10}$SO$_4$, pK$_s$ = 117.5 or pK$_s$ = 116.0 (Singh and Brydon 1969, 1970)
Jurbanite, Al(OH)SO$_4$, pK$_s$ = 17.23 (van Breemen 1973) or pK$_s$ = 17.80 (Nordstrom 1982).

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Impacts of Atmospheric Pollutants on Lake Sediments Since 1940

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ABSTRACT

Geochemical evolution of the most recent sediments from four soft water lakes Tantaré, Bec Croche, Laflamme and Gemma—located on the southern edge of the Laurentides Highlands of the Canadian Shield close to Québec City has allowed us to reconstruct past trends in precipitation acidification for the region studied. Although there is no major anthropogenic activity within the watersheds, it is shown that Pb, Zn, Hg, Ni and Cu levels in the sediments increased significantly from 1940 onwards. However, the reduction in the stratigraphic concentration of Zn and Hg after 1960 in Lake Tantaré, an acidified system, and in the three other non-acidified lakes, might be the result of an important decrease in the total particulate emissions to the atmosphere as a result of new technology and the use of less polluting energy sources. We have estimated that in 1940 the atmospheric transport of heavy metals was close to its natural level and the pH of precipitation was 5.6. It is demonstrated that the pH has since decreased in the region at a varying rate during the last 40 years to reach a low value of 4.2 in 1980. A second core from a deep basin (17.5 m) of Lake Tantaré shows a different stratigraphic progression of several geochemical parameters from the one taken at a shallower (5 m) coring site. For the partially anoxic deeper site, the reduction in Al and Si concomitant with the increase of C within the 0- to 10-cm stratigraphic interval seems to be the result of surface water acidification processes. The increase of C may be attributed to the slower mineralization processes of organic matter and to the increase in the rate of organic matter flocculation in the water column. On the other hand, the reduction of Si (biogenic Si) might well be associated with the reduction of the phytoplanktonic community (Diatoms) which would also explain the unusual high transparency (11 m) for the lake. The varying content of Al in the upper 0- to 10-cm interval is probably the result of chemical processes favouring its mobility.

Snow as an Indicator of Atmospheric Fluoride Contamination

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ABSTRACT

During the month of March 1978, 344 snow samples from the Saguenay - Lac Saint-Jean Region (Québec) were analyzed for fluoride content (F^-, $\mu g\ L^{-1}$). Concentrations of individual samples ranged from <20 to 50 000 $\mu g\ L^{-1}$ with a mean value of 925 $\mu g\ L^{-1}$. The major sources of the pollutant in this area are two aluminum smelters (Alma and Arvida) having an annual production of 74 000 and 435 000 tonnes. Approximate fallout distribution, defined as the area around the aluminum smelters containing snow showing F^- levels of >50 $\mu g\ L^{-1}$, is 3000 km^2. Although the results of the present study concern short-to medium-range transport of F^- within the atmosphere, the study shows the need for work on the long-range transport of F^-, which is an important environmental pollutant. Such work should be carried out in conjunction with other anthropogenic pollutants using routine chemical analytical methods for F^- with a detection limit close to 1 $\mu g\ L^{-1}$.

INTRODUCTION

During the past decade, a considerable number of publications have appeared on the various aspects of environmental impacts due to atmospheric emissions of pollutants. As an example, one can cite the large number of articles concerned with the acidification of surface waters caused by the atmospheric emissions of sulfur and nitrogen oxides (Drablos and Tollan 1980; Ouellet and Jones 1983). On the other hand, it appears that the impact of fluorides on the environment has been relatively neglected. This would seem to be a paradox as fluoride contamination of the atmosphere is ranked as one of the major pollutant problems, along with sulfur and nitrogen oxides and ozone (Marier 1972). Some of the American and German coals used in thermal power-generating plants contain up to 500 $mg\ kg^{-1}$ of fluorine and can give rise to precipitation containing up to 14.1 $mg\ L^{-1}$ of fluoride (Tourangeau et al. 1977; Garber 1970). In the USA, the EPA (1972) has estimated that American industries were emitting annually into the atmosphere in the late sixties over 150 000 t of soluble fluoride. A recent review (Galloway et al. 1980), carried out within the National Atmospheric Deposition Program and dealing specifically with toxic substances in atmospheric deposition, included no discussion on fluoride. In effect, most studies on fluoride have dealt with the various aspects of human, animal and plant health (Gabovich and Ovrutskiy 1970; OMS 1970; NAS 1971; Rose and Marier 1977; Waldbott et al. 1978).

The greater part of dissolved fluoride in surface waters originates from the fluoride content of atmospheric precipitation. This, in turn, arises from three main sources: 1) volcanic activity, 2) industrial emissions and 3) the sea. In Canada, 56% (8000 t) of the annual fluoride atmospheric emissions (14 220 t) originates from the aluminum industry (Environment Canada 1976).

Within the Province of Québec, the contribution of this industry to atmospheric emissions of fluoride amounts to 6870 $t\ yr^{-1}$ (MEQ 1979), which represents about 90% of the total. Cryolite (Na_3AlF_6) is used in the electrolytic processing of alumina as a fusing agent. At the fusion temperature of the metal some fluorides are volatilized and escape to the atmosphere.

SITE DESCRIPTION

Within the Saguenay - Lac Saint-Jean Region, there are three aluminum smelters owned and operated by ALCAN with a potential production of close to 700 000 t yr^{-1}. The Arvida plant, the largest in the world, has a production capacity of 435 000 t yr^{-1}, while the one at Alma (Isle Maligne) produces 74 000 t of aluminum per year. These two plants have been in operation for several decades. The Grande-Baie smelter is the newest plant in Canada and emits substantially lesser amounts of atmospheric fluoride than those at Arvida and Alma. It became operational in 1981 and has a maximum annual production capacity of 189 000 t. The energy needed to operate these three aluminum plants is produced in the Saguenay - Lac Saint-Jean catchment area by six hydro-electric stations developing a total power of 2 700 MW, which is about 10% of the total Québec hydro-electric power currently generated by the provincial network (excluding the Québec-Labrador 4500 MW).

METHODS

In March 1978, 344 snow samples were collected within an area of 4500 km^2 situated in the regional lowlands of the Saguenay River from the east shore of Lac Saint-Jean to the Ha! Ha! Bay (Figure 1). Individual sites were in open ground well removed from the main roads in both urban and rural situations. Samples were taken with a small plastic scoop, placed in plastic bags and kept frozen (-20°C) until melted for laboratory analysis. The fluoride (F^-) content of each sample was estimated by means of an ion analyzer (Orion Research, model 801A) coupled to a F^- selective electrode (Orion, model 94-09 (EPA 1974)). The detection limit of the method is 20 $\mu g\ L^{-1}$ and the reproducibility of the results ± 2%.

RESULTS

The F^- content of the snow cover (Figure 1) reflects the fallout pattern of F^- from the Arvida and Alma smelters. Mean F^- content is 925 $\mu g\ L^{-1}$; a maximum of 23 mg L^{-1} was recorded close to the two plants in March at a site which, during a preliminary sampling expedition in February, had shown a maximum concentration of 50 mg L^{-1}. The fallout area (3000 km^2) has a west to east elongation, as a result of the westerly winds which are dominant in this region, and the presence of high land ($<$ 200 m) immediately to the north and south of the sampling area.

These results may be partially correlated with those from the phytosociological studies of Leblanc et al. (1971, 1972); these authors demonstrated that communities of lichens and mosses were adversely affected in a northerly direction up to a distance of 12 km from the aluminum plants. In addition, fluorose in dairy cattle has been identified in this region since 1951 and a sum of approximately $3 million has been received from ALCAN by farmers as compensation for the loss of production (MEQ 1979).

Unfortunately, the global environmental impacts of these atmospheric fluoride emissions, which began in 1926, are still largely unknown. Preliminary dendrochronological studies are now being carried out in the area shown in Figure 1 to evaluate if there are adverse effects on tree growth. No study has been undertaken to estimate the threat to the health of the population either now or formerly living within the polluted area.

It must be noted, however, that since 1972 the progressive installation of antipollution devices at both the Arvida and Alma plants has contributed substantially to the reduction of fluoride emissions. The new smelters of Grande-Baie, first operational in 1981, seem to give cleaner emissions (Bouchard et al. 1981; Paquet 1983).

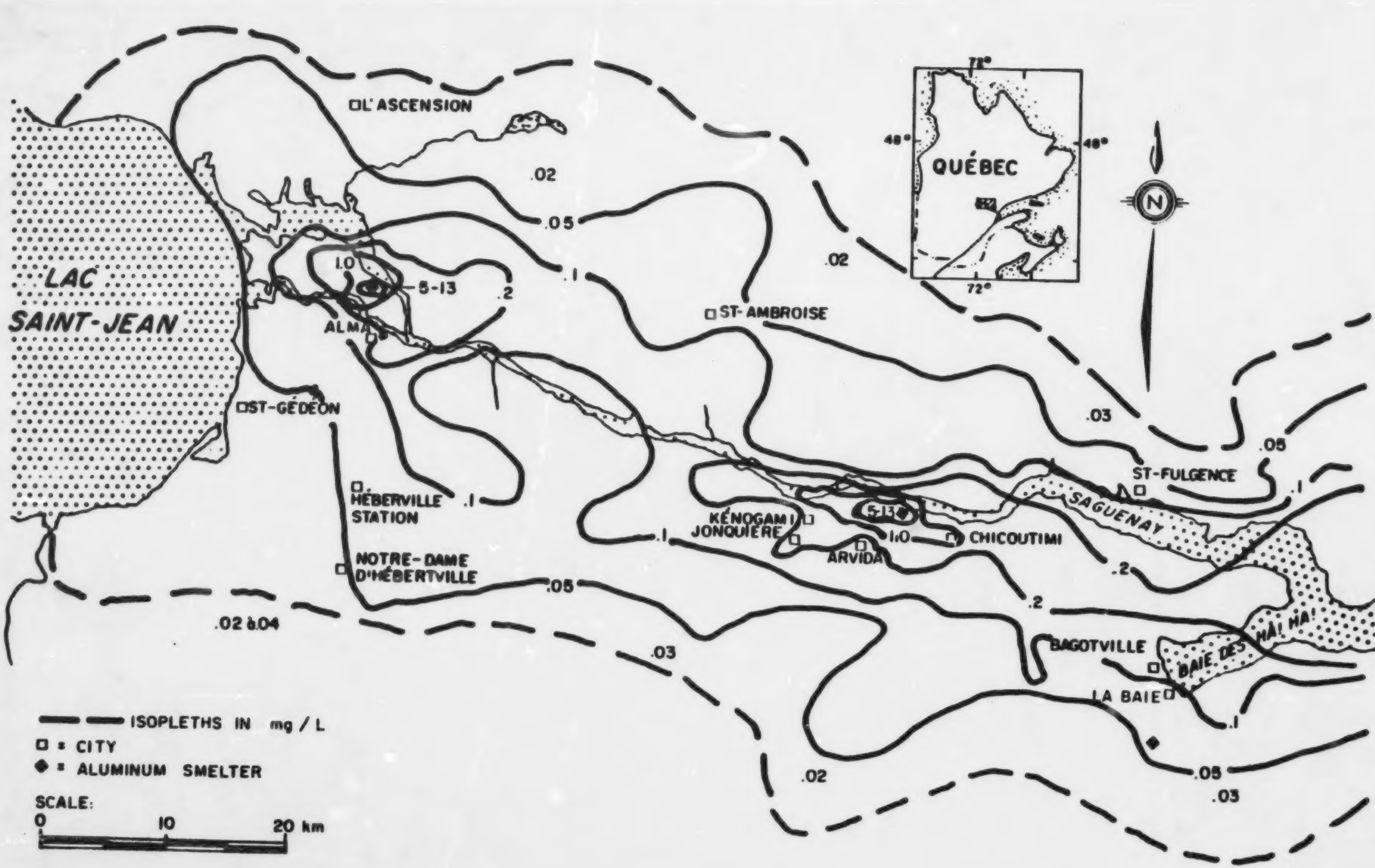
LAC SAINT-JEAN
L'ASCENSION
QUÉBEC
48°
48°
72°
72°
N
.02
.05
.1
.2
1.0
5-13
ALMA
ST-AMBROISE
.02
.03
.05
.1
ST-GÉDÉON
HÉBERVILLE STATION
.1
NOTRE-DAME D'HÉBERTVILLE
.05
.02 à.04
.03
KÉNOGAMI
JONQUIÈRE
5-13
1.0
ARVIDA
CHICOUTIMI
ST-FULGENCE
SAGUENAY
.2
.2
BAGOTVILLE
BAIE DES HA! HA!
LA BAIE
.1
.05
.03
.02
ISOPLETHS IN mg / L
□ = CITY
◆ = ALUMINUM SMELTER
SCALE:
0
10
20 km

Figure 1. Fluoride distribution in snow of the Saguenay - Lac Saint-Jean Region, Québec, for the month of March 1978.

The fallout area shown in Figure 1 is the typical result of a case study on the short-range transport of an atmospheric pollutant the sources of which are easily identifiable. It cannot be compared scale-wise to the long-range atmospheric transport of acidic pollutants such as SO_4^{2-} and NO_3^- for which the emission sources are varied and the transport distances of the order of thousands of kilometers.

The toxic nature of the fluoride ion does, however, raise two questions: first, whether the various aluminum plants, brickworks and power stations in industrialized areas can contribute to the long-range transport of F^- on a continental scale; and secondly, whether F^- levels after such long-range transport are of sufficiently high levels to cause concern. Very little on the environmental chemistry of fluorine is known, and data on the reservoirs and fluxes of this element in global cycles are very sparse. Table 1 shows the absolute abundance and relative abundance ($Al = 1$) of the elements associated mainly with the lithologic reservoirs (Al, Fe, Ca; soil, rocks, coal), hydrologic reservoirs (Ca, Cl; fresh and sea water) and the atmospheric reservoirs (precipitation, air) in global chemical cycles. The table shows clearly how chlorine is enriched in the atmosphere and hydrosphere in comparison to the lithologic reservoirs and indicates that the main pathway of this element is atmospheric transport, precipitation and surface water transport between the land and sea masses.

Although we have no comparable data on the mean background content of F^- in precipitation, an estimation may be possible by considering the respective origins and chemical characteristics of Cl^- and F^- aerosols in the atmospheric reservoir. In this way, a subsequent evaluation of a mean washout ratio for the fluoride ion may be made (the apparent mean washout ratio of Cl^- calculated from Table 1 is 2.78×10^5). If we assume that the source of F^- in the atmosphere is sea water and that the phenomena giving rise to Cl^- aerosols also give rise to F^- aerosols, then one would expect from the respective concentrations of Cl^- and F^- in sea water that the mean background level of F^- from this source in the atmosphere would be $0.12\ ng\ m^{-3}$,. This value is much closer to the mean value for Europe ($1.5\ ng\ m^{-3}$) more strongly influenced by maritime winds than that for the continental air masses of northeastern America ($10\text{-}400\ mg\ m^{-3}$). This suggests that the anthropogenic component of the total fluorine loading in the atmosphere of the latter region is the dominant part. The fluorine-containing aerosols may thus not have any similarity to chlorine aerosols and the respective washout characteristics may be different. However, if F^- is emitted as a submicron aerosol in an acidic environment it will tend to associate more with acidic sulphate and nitrate aerosols than with clay particles where it could be fixed in non-exchangeable form by the replacement of OH groups. This latter process would lead to short-and medium-range transport of F^- around emission sources rather than transport over longer distances. In contrast, F^- either associated with submicron acidic aerosols (NH_4^+, SO_4^{2-}, H^+, NO_3^-) or in the vapor phase (HF) could be transported over long distances and, in the event of suitable precipitation episodes, show high washout ratios of $\approx 10^4\text{-}10^6$ (Scott 1981). If this is so, then the global background value of F^- expected in the precipitation for rural areas (Table 1) from the long-range transport of this element should range from 0.1 to 10.0 $\mu g\ L^{-1}$ in eastern North America, which is in accordance with the mean value of 8.1 $\mu g\ L^{-1}$ found by Barnard and Nordstrom (1982). Similarly from urban-area data and assuming a maximum washout ratio of 10^6, it can be expected that the concentration of F^- in the precipitation in polluted areas would attain $> 400\ \mu g\ L^{-1}$. These projected values for the concentration of F^- in precipitation subsequent to either long-range transport or regional pollution would require that the study of F^- with other aerosols of anthropogenic origin be carried out using routine analysis of the ion within the 1-10 $\mu g\ L^{-1}$ range. Whether exposure of plant and animal populations to such incident levels of F^- in the atmosphere can have adverse effects on community structures awaits demonstration. The present slowing of growth and the die-back of the German Black Forest, which is now turning yellow (Toufexis 1984), as well as other forest (Ulrich et al. 1980; Bormann 1982), might well be partly related to the fluorine atmospheric pollutant as well as to the acidifying products.

CONCLUSION

The F^- analysis of snow samples from the Saguenay - Lac Saint-Jean Region shows a highly polluted fallout area around the two main aluminum smelters in the area. Although data are not available on background levels of F^- in eastern North America, a consideration of F^- concentration in the air masses of this region and an estimation of the approximate range of values for the potential washout ratios of F^- aerosols lead to possible background levels of from 0.1 to 10 $\mu g\ L^{-1}$ for F^- in the precipitation for this area. Actual F^- levels in the fallout area average, in 1978, 925 $\mu g\ L^{-1}$, which indicates that this region was receiving extreme pollution loadings of this element.

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Table 1. Mean concentrations of Al, Ca, Fe, Cl and F in the main reservoirs of global chemical cycles

Reservoirs	Al	Ca	Fe	Cl	F	Reference
Atmosphere* (ng m^{-3})	2×10^3 (1)	2.8×10^3 (1.4)	3.6×10^3 (1.8)	1.8×10^3 (0.9)	rural, 10 (0.005) urban, 400 (0.2)	1
Precipitations (µg L^{-1})	10 (1)	5×10^2 (50)	15 (1.5)	5×10^2 (50)	rural, 2 (0.2) urban, 20 (2)	2, 4
Freshwater (µg L^{-1})	3×10^2 (1)	1.5×10^3 (50)	5×10^2 (1.6)	7×10^3 (23.3)	1.5×10^2 (0.5)	1, 5
Seawater (µg L^{-1})	2 (1)	412×10^3 (206×10^3)	2 (1)	19.4×10^6 (9.7×10^6)	1.35×10^3 (0.67×10^3)	1
Soil (mg kg^{-1})	71×10^3 (1)	15×10^3 (0.21)	40×10^3 (0.56)	1×10^2 (0.001)	2×10^2 (0.003)	1
Rock (mg kg^{-1})	82×10^3 (1)	41×10^3 (0.5)	41×10^3 (0.5)	13×10^2 (0.002)	9.5×10^2 (0.01)	1
Coal (mg kg^{-1})	12.9×10^3 (1)	7.7×10^3 (0.6)	19.2×10^3 (1.5)	1.4×10^3 (0.11)	61 (0.005)	3

* Northeastern America

( ) geochemical ratio, element/aluminum (w/w)

1: Bowen, A.J.M. (1979).

2: Tanaka, S., Darzi, M., Winchester, J.W. (1981).

3: Flanagan, R.C., Friedlander, S.K. (1978).

4: Barnard, W.R., Nordstrom, D.K. (1982).

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Acid Rain, Drought, and Red Spruce Growth Responses

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ABSTRACT

Incremental growth cores were collected from red spruce (*Picea rubens* Sarg.) trees growing on bedrock and on glacial till at the Hubbard Brook Experimental Forest, West Thornton, New Hampshire. Results of regression analyses of tree growth indices against orthogonally transformed temperature and precipitation data for two time periods, 1932-1956 and 1956-1980, indicate that the relationship of tree growth to climate has been altered. For trees growing over bedrock the variance explained by climate decreased from 56.9 to 23.5% and the variance due to prior growth decreased from 19.6 to 15.5%. For trees growing over glacial till the variance explained by climate decreased from 65.4 to 8.2% and the variance due to prior growth increased from 2.3 to 66.4%. Statistical t-tests and F-tests of climate data for the two periods indicate that climate has been essentially the same from 1932 through 1980. The Palmer Drought Index indicates that droughts have occurred in 60% of the last 50 years with a peak magnitude in the mid-1960s. It has been shown that the hydrogen ion component of acid rain is neutralized through dissolution of reactive alumina in glacial till soils. The toxic Al^{3+} thus generated may then damage the root systems of red spruce. However, as a result of the formation of organometallic complexes in the humus layer of the glacial till soils, roots in the humus layer may not be damaged, thereby effectively restricting root systems of trees growing on glacial till to the humus layer. The root systems of trees growing in thick humus over bedrock would not be damaged to the same extent. During prolonged dry periods such as occurred during the 1960s, trees with restricted root systems would be more severely stressed than trees physiologically acclimated to growing in humus over bedrock.

INTRODUCTION

Dieback and decline of red spruce (*Picea rubens* Sarg.) in the northeastern United States has been documented by several investigators (Siccama et al. 1982; Vogelmann 1982; Johnson and Siccama 1983) and, although considerable research on the subject has and is being conducted, the primary causative factors remain undetermined. However, Johnson and Siccama (1983) have shown that red spruce decline is positively correlated with increasing elevation, suggesting a possible relationship with environmental factors which increase with elevation, such as: (i) acidic deposition, (ii) precipitation and cloud moisture, (iii) leaching of nutrient ions from plant surfaces, (iv) heavy metal accumulation, and (v) wind speed; or those which decrease with elevation, such as (i) temperatures, (ii) soil base status, (iii) soil pH, and (iv) soil moisture-holding capacity. Of the numerous natural and anthropogenic factors which have been considered as primary initiatory stresses, the two currently in vogue are acid rain and drought. Johnson and Siccama (1983) have established that red spruce decline is characteristic of stress-related disease. Uncertainty remains as to whether the stress involved is of a chronic low-level type (such as acid deposition) or a more devastating episodic event (such as extreme drought). In this report the results of statistical analyses of growth measurements of red spruce trees growing in the White Mountains of New Hampshire are discussed in light of current hypotheses regarding red spruce decline.

MATERIALS AND METHODS

Site Description

Both study sites (Fig. 1) are within 2 km of the Hubbard Brook Experimental Forest headquarters building, West Thornton, New Hampshire (43°57'N, 71°42'W; 252 m). Climate of the area is continental with average precipitation of about 1300 mm per year (Bormann and Likens 1979) and mean temperatures of 19°C in July and -9°C in January (Federer 1973). Bedrock is sillimanite-zone gneiss of the Littleton Formation, which is quartz, plagioclase, and biotite. Glacial till of similar composition covers much of the bedrock (Johnson et al. 1968). Soils developed on the till are mostly spodosols averaging about 0.5 m in depth, overlaid with a 3-to 15-cm-thick mor humus layer (Bormann and Likens 1979). Most of the Hubbard Brook watershed was logged between 1900 and 1917 with red spruce reportedly cut around 1909 (Bormann et al. 1970).

Site I is located approximately 1.3 km southeast of the Hubbard Brook headquarters building at an elevation of 335 m on a south to north-trending exposed bedrock ridge. The tree stratum at this site consists mostly of red spruce (*Picea rubens* Sarg.) and a few white pine (*Pinus strobus* L.) growing in a humus layer over bedrock. Humus thickness was variable with 30 cm being the maximum observed. Maximum age of the 20 trees sampled was 123 years in 1981. Site II is located approximately 2 km northwest of the headquarters building at an elevation of 550 m on a south-facing till slope. Beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), yellow birch (*Betula alleghaniensis* Britton), basswood (*Tilia americana* L.), red maple (*Acer rubrum* L.), and red spruce were all present over the site. Trees growing at this site were rooted in humus and glacial till and, for the 14 trees sampled, the maximum age was 122 years in 1981.

Methods

Climate data consisted of monthly mean temperature and precipitation of the southern New Hampshire climatic division for the period 1931-1980. Divisional climate data was used for two reasons: (1) local records of sufficient length were unavailable and (2) divisional data may be more representative of the macroclimate to which the trees are responding than a station record only a few tens of kilometres away (Blasting et al. 1981). Also because of the averaging process, heteroscadascity in individual station data may be smoothed out. The temperature and precipitation data were divided into two periods, 1932-1956 and 1956-1980, and were checked for homogeneity between the periods. Statistical F-tests and t-tests were used to test the null hypotheses that the variances and means, respectively, of the monthly climatic variables for the two periods were equal. In those cases where the variances were not equal, an approximate t-statistic was calculated and Satterthwaite's approximation was used to compute degrees of freedom (Helwig and Council 1979).

Measurements were made of annual-ring widths of each increment core collected (two cores per tree) from the 20 trees at Site I and the 14 trees at Site II. From them, tree growth data were calculated. Annual-ring widths of each core were measured to the nearest 0.01 mm. Each core chronology was then standardized to remove non-climatic trends and correct for heteroscadascity. Standardization was done by fitting a trend line to the data followed by dividing ring widths by their corresponding trend-line values. The resulting time series were then averaged year by year to produce an average tree-ring index chronology for each site.

Response-function analysis (Fritts et al. 1971; Fritts 1976; Puckett 1982) was then used to determine the relationship of tree growth to climate. This procedure involves regressing tree growth indices on prior growth data and factor scores calculated from monthly climate data. Each response-function year included monthly climate data for April-September of the previous year, October-March of the preceding fall and winter, and April-September of the current year. In addition to monthly climate data, up to three years of prior tree growth data were available for selection in the multiple regression procedure. By subtracting the percent variance explained by climate alone from the percent variance explained by climate and prior growth, it is possible to estimate the percent variance explained by prior growth alone. The response-function equations derived in the multiple regression procedures were then used to predict tree growth from which residuals were calculated.

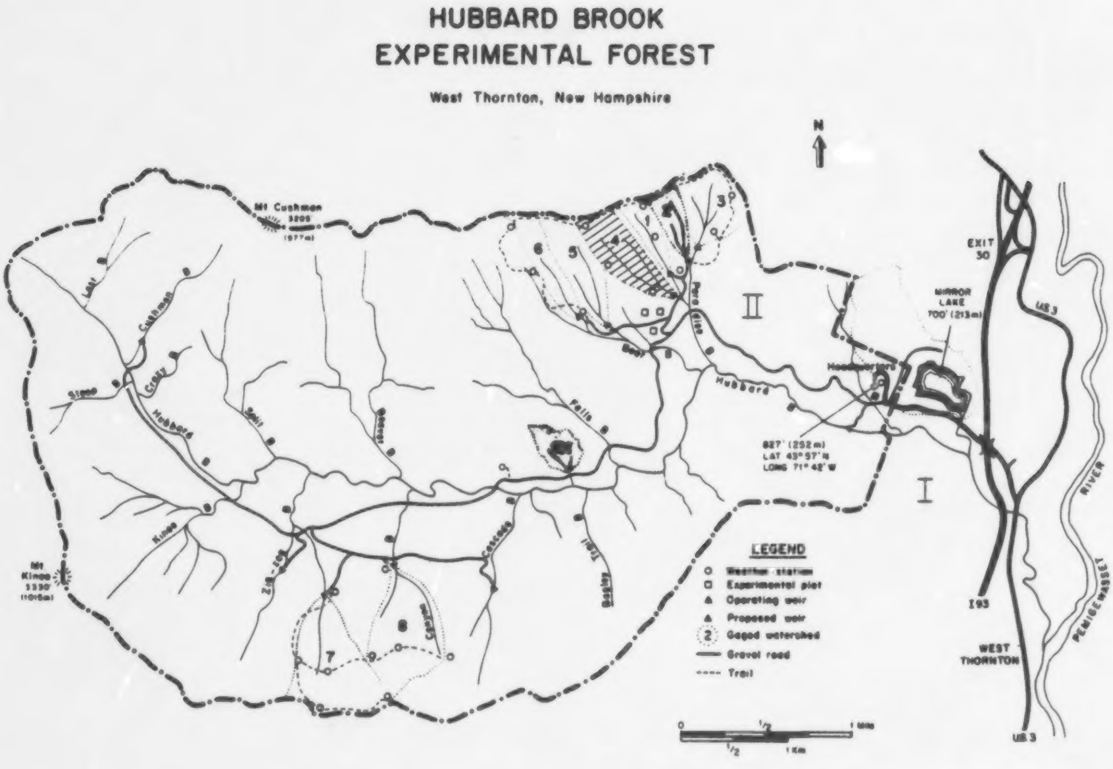
HUBBARD BROOK
EXPERIMENTAL FOREST
West Thornton, New Hampshire
N
Mt Cushman 3205 (977m)
Mt Kineo 3330 (1016m)
Lost B
Cushman B
Crazy B
Sleepe
Hubbard
Bell B
Kineo
Zig-Zag
Steep
Falls B
Cascade
Canyon
Beaver
Paradise B
Bear B
Hubbard
Headquarters
MIRROR LAKE 700' (213m)
EXIT 30
US 3
827' (252 m)
LAT 43° 57' N
LONG 71° 42' W
II
I
1
2
3
4
5
6
7
8
LEGEND
Weather station
Experimental plot
Operating weir
Proposed weir
Gaged watershed
Gravel road
Trail
0
1/2
1 Mile
1/2
1 Km
I93
WEST THORNTON
US 3
PEMIGEWASSET RIVER

Figure 1. Map showing red spruce collection sites in and near the Hubbard Brook Experimental Forest, West Thornton, New Hampshire. Site I is about 1.3 km southeast of the Hubbard Brook headquarters building at an elevation of 335 m and Site II is adjacent to experimental watershed 3 at an elevation of 550 m.

In order to determine whether any change may have occurred in the relationship of tree growth to climate over the past 50 years, response functions were calculated for two periods, 1932-1956 and 1956-1980. The F-ratio (the ratio of regression mean squares to the error mean squares) and the R^2 (the coefficient of determination) for a particular regression step were used as statistical estimates of the strength or significance of the relationship of tree growth to climate (Sokal and Rohlf 1969; Puckett 1982). Ezekial and Fox's (1959) procedure was followed to adjust the R^2 for lost degrees of freedom. If anthropogenic emissions and acidic deposition have indeed resulted in increased environmental stress it was assumed that this would be reflected in alterations of the response-function results over time.

RESULTS AND DISCUSSION

Means and variances of the climate data for the two experimental periods (1932-1956 and 1956-1980) are presented in Table 1. Results of the climate data tests indicate that the variances and means of the temperature data and the means of the precipitation data are not significantly different. Of the precipitation data variances only three months, February ($P = 0.021$), March ($P = 0.001$), and December ($P = 0.017$), were significantly different. This suggests that, with minor exceptions, the climate of the two time periods was statistically similar enough to have been drawn from the same population. It seems safe, therefore, to assume that any changes in the relationship of tree growth to climate could not be due directly to changes in climate.

Table 1. Means and variances (in parentheses) of New Hampshire temperature and precipitation for the 1932-1956 and 1956-1980 periods

	Temperature		Precipitation	
	1932-1956	1956-1980	1932-1956	1956-1980
January	16.0(24.0)	14.0(19.4)	3.02(1.17)	2.67(2.25)
February	17.0(17.6)	15.4(16.0)	2.42(0.40)	2.53(1.02)
March	26.1(22.1)	26.5(14.4)	3.39(3.24)	2.73(0.76)
April	39.2(10.2)	38.9(6.8)	3.45(1.39)	2.97(0.76)
May	51.7(7.3)	51.7(10.2)	3.94(2.11)	3.36(1.56)
June	61.2(2.3)	60.8(3.6)	4.20(2.59)	4.15(2.43)
July	65.9(4.0)	65.1(4.0)	4.32(1.96)	3.99(1.85)
August	63.8(6.8)	63.0(5.3)	3.61(1.72)	4.16(2.37)
September	55.8(5.3)	55.2(6.3)	4.31(3.39)	3.32(1.80)
October	45.9(7.3)	44.8(7.3)	3.38(2.25)	3.73(2.25)
November	33.4(12.3)	33.4(9.6)	3.86(2.50)	3.85(1.64)
December	19.7(16.8)	19.0(20.3)	3.25(1.12)	3.41(3.03)

Multiple regression response-function results for red spruce at both sites and time periods were markedly different (Table 2). Trees growing at Site I showed a strong relationship with climate ($R^2 = 0.569$) for the 1932-1956 period. However, this relationship decreased considerably during the 1956-1980 period ($R^2 = 0.235$). Prior growth at Site I accounted for 19.6% of the variance in tree growth for the 1932-1956 period but only 15.5% for the 1956-1980 period. The multiple regression equation accounted for a total of 76.5% of the variance in tree growth ($R^2 = 0.648$) for the 1932-1956 period and only 39.0% of the variance ($R^2 = 0.335$) for the 1956-1980 period.

Table 2. Response-function results for red spruce at each site and time period

	Site I		Site II	
	1932-1956	1956-1980	1932-1956	1956-1980
Percent variance due to climate	56.9	23.5	65.4	8.2
Percent variance due to prior growth	19.6	15.5	2.3	66.4
Total variance explained (R^2)	76.5	39.0	67.7	74.6
Adjusted R^2	64.8	33.5	56.9	67.9
F-ratio	5.42**	4.48*	5.09**	8.80***
Number of variables	9	3	7	6
Residual degrees of freedom	15	21	17	18

*,**, *** $P < 0.05, 0.01, 0.001$, respectively.

Red spruce growing at Site II also showed a strong relationship ($R^2 = 0.654$) with climate during the 1932-1956 period. However, this decreased dramatically during the 1956- 1980 period ($R^2 = 0.082$). The influence of prior growth was inversely similar: the percent variance in tree growth accounted for by prior growth increased from 2.3% during the 1932- 1956 period to 66.4% during the 1956-1980 period. The total variance explained by the multiple regression equations increased slightly, accounting for 67.7% ($R^2 = 0.569$) of the variance in tree growth during 1932-1956 and 74.6% ($R^2 = 0.679$) during 1956-1980.

From the comparisons of the multiple regression results, it is apparent that changes have occurred in the manner in which trees are responding to the macroclimate. It seems especially noteworthy that the alteration of the relationship of tree growth to climate differed at the two sites. This may be due in part to the quite different physical properties of the sites. Site I with its xeric soil properties and exposed location is considered to be near the tolerance-range limit for red spruce and therefore physiologically a high-stress site. Site II, on the other hand, is considered to represent the more mesic conditions of the northern hardwood forest with a much lower level of physiological stress. The theoretical relationship between increasing environmental stress and the correlation of tree growth with climate is shown graphically in Fig. 2. Based on this relationship, the correlation between tree growth and climate should increase as environmental stress increases. Once the response threshold is reached at the inflection point (Fig. 2), the correlation between tree growth and climate will decrease as stress increases.

From the response-function results it appears that the a priori assumption of greater stress at Site I is not valid since, for the 1932-1956 period, the percent variance explained by climate at Site I (56.9%) is less than at Site II (65.4%). However, with respect to Fig. 2, if we assume that trees at Site I are at point C and the trees at Site II are at point B, then the a priori assumption of greater stress at Site I is valid. The response-function results, for the 1956-1980 period, suggest that with respect to Fig. 2 the trees at Site I have moved from point C to point D (23.5% variance explained by climate) and the trees at Site II have moved from point B to point E (8.2% variance explained by climate). This implies that environmental stress has increased more at Site II (the B-E shift) than at Site I (the C-D shift).

Along with the alteration of the relationship of tree growth to climate was a change in the importance of prior growth. For trees growing at Site I the percent variance explained by prior growth decreased slightly, whereas at Site II it increased dramatically. As a general rule (Fritts 1976) high prior growth response values such as for Site II (1956-1980) indicate that there is very little year-to-year variation in tree growth in response to year-to-year fluctuations in climate. Therefore, annual-ring width in one year will be almost the same as in prior years. Such a situation may arise due to (1) the trees reaching such a large diameter that only a few cells are added each year, (2) an extreme reduction in environmental stress such that the trees attain their maximum growth potential without annual fluctuations, or (3) an extreme increase in environmental stress such that the trees are no longer physiologically capable of responding to climate. It is highly unlikely that any of the trees growing at Site II have reached sufficient diameter to bring about such a change in tree growth. Also, because there has been no statistically significant change in climate or disturbance at Site II during the 1931-1980 period, it seems equally unlikely that environmental stress has declined. The remaining hypothesis for the observed change in tree growth, therefore, is that there has been an increase in environmental stress of sufficient magnitude to limit tree growth physiologically.

Drought

Several researchers have commented on the potential involvement of extreme drought in red spruce dieback (Roman and Raynall 1980; Siccama et al. 1982; Johnson and Siccama 1983). Red spruce is relatively shallow-rooted with an average root depth of 33 cm (Fowells 1965), a factor which could predispose the species to drought sensitivity. Although the climate-data tests did not indicate any significant change in climate, there have been several droughts (1941, 1949-1950, 1957, 1959, 1963-1966, 1980) in New Hampshire during the 1931-1980 period (Fig. 3) with the most severe occurring in 1963-1966. Droughts of a sustained nature are potentially the most harmful since the humus and shallow soil zones may completely dry out, resulting in the death of the fine and small roots growing there. This represents an indirect effect of climate on tree growth in that, depending on the degree of root damage, it may take several years for the root system and, therefore, the trees themselves, to recover. During this recovery period tree growth may be less than expected. From examination of the residuals of tree growth calculated for both Site I and Site II (Fig. 4) it is apparent that droughts may have had some effect. This seems particularly true for the 1941 and the 1963-1966 droughts. However, at both sites the negative residuals seem only to coincide with the actual drought periods. They do not persist for several years as would be expected if the root systems were severely damaged.

As was previously discussed, it is assumed that Site I is a more physiologically growth-limiting site than Site II. Because trees growing at Site I are rooted primarily in a discontinuous humus mat and those at Site II are rooted in both humus and deep glacial till the Site I trees would seem more susceptible to drought damage. It therefore follows that if drought was the cause of an alteration in tree growth, it should have been more pronounced at Site I. Drought alone, therefore, seems to have played little if any part in the observed alteration of the relationship of tree growth to climate. This is the same conclusion reached by Siccama et al. (1982) regarding the role of drought in spruce dieback. They pointed out that soil moisture measurements at Camels Hump, Vermont, during the summers of 1964-1967, showed both the humus and shallow mineral soil horizons stayed above field capacity during those drought years. Also, unpublished data from regression analyses of the relationship between tree growth and precipitation and streamflow at Hubbard Brook indicated that tree growth on "rocky acidic till soils" is better in dry years than in wet years. This information was offered as evidence of the unlikelihood of a link between drought and spruce dieback. This evidence is particularly interesting since, as previously discussed, it was the Site II spruce growing on till soil that showed the greatest alteration in growth responses.

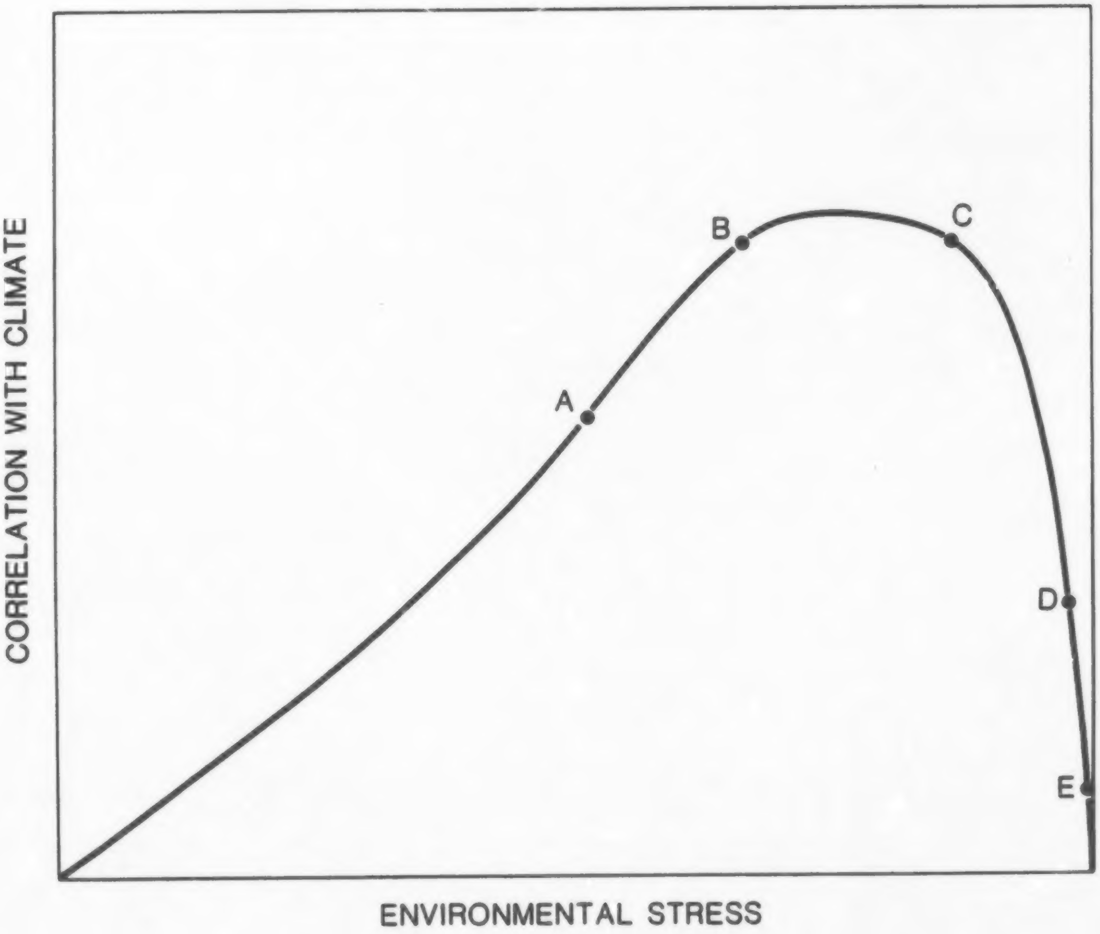

Figure 2. Theoretical relationship between environmental stress and the correlation of tree growth with climate

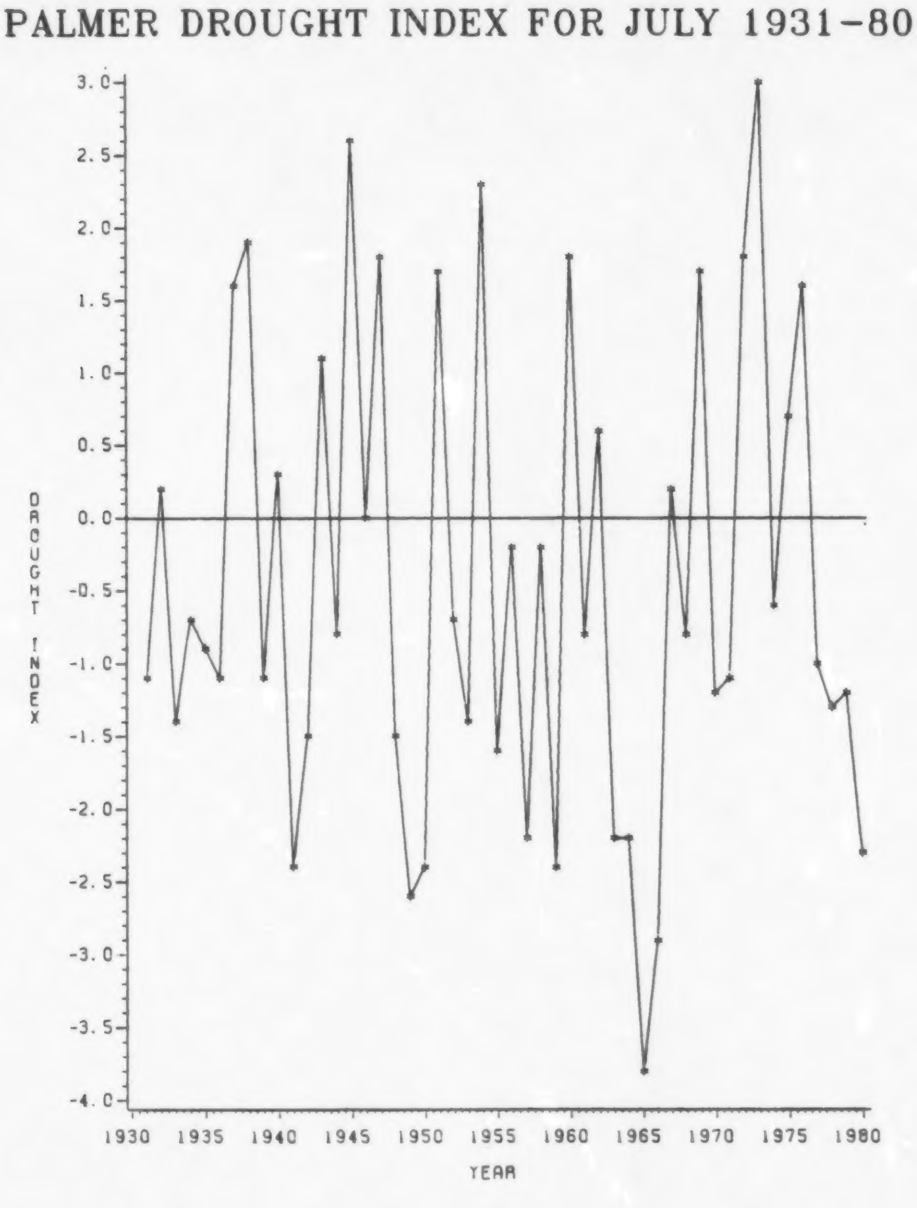

Figure 3. New Hampshire Palmer Drought Index values for July, 931-1980.

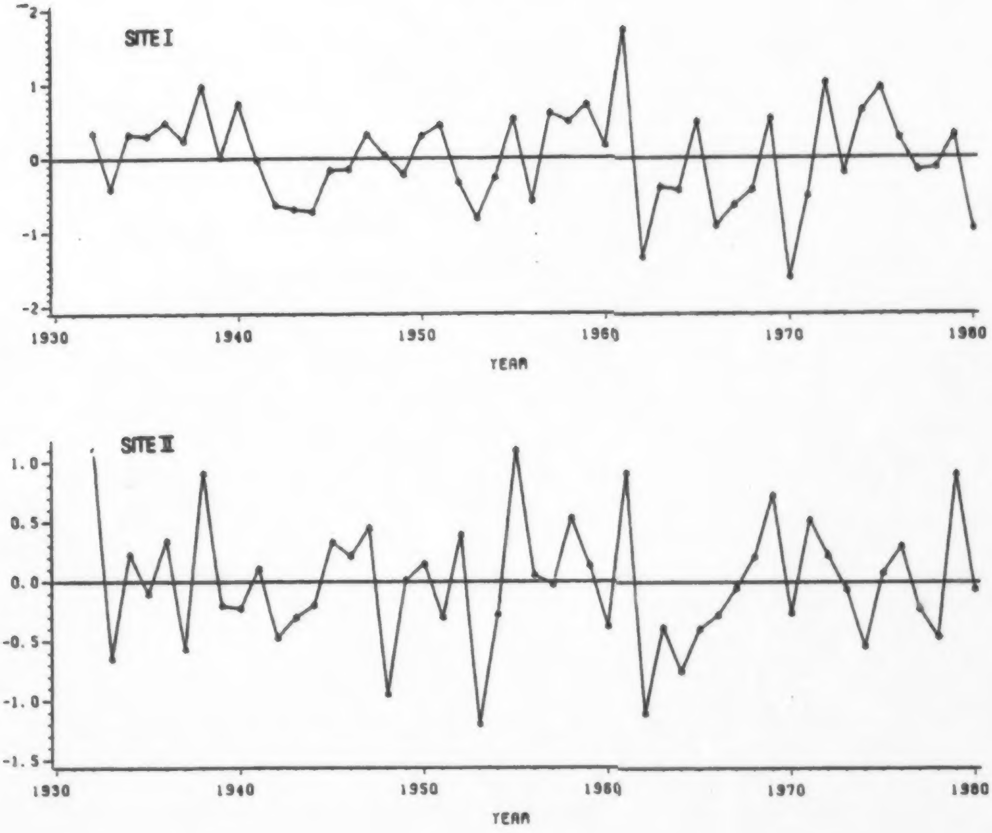

Figure 4. Residuals of tree growth, 1932-1980, at Site I and Site II as calculated in the multiple regression, response-function procedures.

Johnson and Siccama (1983) have suggested that drought may have been a predisposing stress factor in the initiation of spruce dieback, particularly at high-elevation sites where the moisture-holding capacity of the soil is diminished. From their study of red spruce stands along both latitudinal and elevational gradients it appears that the dieback phenomenon is most advanced in high-elevation, northern Appalachian stands. In fact, there is strong evidence of a positive relationship between spruce dieback and elevation. Johnson and Siccama's evidence of a relationship between spruce dieback and drought is based primarily on their reported absence of dieback symptoms in southern Appalachian stands, which supposedly were not subjected to the mid-1960s drought. This argument now seems open to question in light of recent surveys of spruce stands in the Smokey Mountains, which provide evidence of spruce dieback there (McLaughlin 1983, personal communication). Also from July values of the Palmer Drought Index (Table 3) for states along Johnson and Siccama's latitudinal gradient, we can see that red spruce in some of the healthy southern Appalachian stands were subjected to droughts of equal or greater magnitude than those in the north. Some factor other than drought would, therefore, seem to be implicated as a primary initiating factor in spruce dieback and decline.

Table 3. July, 1961-1966, values of the Palmer Drought Index (PDI) for each of the state climate divisions where red spruce stands were evaluated by Johnson and Siccama (1983)

		Palmer Drought Index					
State/Site	Division	1961	1962	1963	1964	1965	1966
New Hampshire							
White Mountains	2	-0.65	0.48	-1.91	-1.51	-3.59	-2.08
Vermont							
Green Mountains	2	0.65	-1.80	-2.79	-3.75	-5.69	-2.44
New York							
Mt. Whiteface	1	2.48	-1.10	-1.63	-1.94	-2.95	-1.28
Catskills	2	1.92	-2.71	-1.84	-2.36	-5.35	-3.03
Virginia							
Shenandoah	5	0.73	-0.30	-3.36	-3.82	-2.03	-3.86
Mt. Rogers	6	1.28	1.67	-2.18	-2.59	-0.64	0.29
West Virginia							
Monongahela NF	4	1.71	-1.37	-1.18	-3.39	-3.33	-5.58
North Carolina							
Roan Mt.							
Mt. Mitchell	1	1.08	-0.39	-0.19	0.12	-0.46	-1.45

Acid Rain

The possibility that acid deposition may affect tree growth, as well as tree decline, has been the subject of several recent reports (Strand 1980; Roman and Raynal 1980; A.H. Johnson et al. 1981; Puckett 1982; Siccama et al. 1982; Bauch 1983; Johnson and Siccama 1983; Tomlinson 1983; Ulrich 1983). Two classes of mechanisms, direct and indirect, through which acid rain may affect tree growth have been defined (Tamm and Cowling 1976). Direct mechanisms include leaching of nutrient ions from plant tissues, erosion of cuticular waxes, damage to epidermal appendages, and alteration of stomatal function and physiological processes such as photosynthesis (Jacobson 1980). Indirect mechanisms include leaching of nutrient ions from soils, interference with nitrogen fixation and litter decomposition, mobilization of toxic metals, and soil acidification (Seip and Freedman 1980). There is very little experimental evidence that any of these factors are, at present, inducing stress in forest trees. However, Rehfuess et al. (1983) have reported that the dieback of Norway spruce (*Picea abies* Karst.) in Bavaria appears related to Mg and Ca deficiencies, which may be induced by accelerated leaching of these nutrients from the needles. Bauch (1983) has provided evidence that Norway spruce and fir (*Abies alba* Mill.) in Germany have been declining for as long as 30 years. Trees growing in acid soils ($pH < 4.0$) had fine roots deficient in Mg and Ca, and no Al in the cortex, suggesting a relationship to changes in soil chemistry and/or root function. Bauch pointed out that drought stress enhanced the decline phenomenon but did not appear to be the cause.

Changes in soil chemistry, resulting from acidic deposition, have been advanced as the cause of forest stress by several researchers in both Europe (Ulrich et al. 1980; Ulrich 1983) and North America (Vogelmann 1982; Molitor and Raynal 1982; Tomlinson 1983). Alteration of soil chemistry is hypothesized to include both leaching of nutrient cations by excess sulfate and mobilization of toxic metals as soil acidity increases (Johnson et al. 1982). Mobilization of Al^{3+} has been of particular interest in light of reports by Ulrich et al. (1980) and Vogelmann (1982) linking this toxic metal to forest declines in both North America and Europe. However, this theory has met growing skepticism in view of reports by Johnson and Siccama (1983) and Rehfuess (1981) which suggest that the decline of conifers on calcareous soils does not appear related to Al^{3+} toxicity.

The results of this investigation are not inconsistent with the Al^{3+} toxicity theory. Cronan and Schofield (1979) have shown that Al^{3+} is being mobilized in shallow mineral soils in New England. Also, N.M. Johnson et al. (1981) have shown that in the Hubbard Brook area the H^+ component of acid deposition is neutralized by dissolution of reactive alumina in glacial-till soils. Trees rooted in the glacial-till soil horizon such as at Site II may be subject to root damage whereas those rooted primarily in humus such as at Site I may not be equally affected. Aluminum toxicity is known to affect the fine roots of many plant species, leaving the plant unable to take up water. Vogelmann (1982) has reported that copper, lead, and zinc also may induce this effect in red spruce. If the fine roots of red spruce at Site II have been negatively affected by Al^{3+} in the mineral soil, this would leave the trees dependent on the fine roots in the organic horizon for most of their water and nutrient uptake. Roots of trees in the organic horizon at Site I and Site II would not be as likely to suffer Al^{3+} toxicity due to the formation of organo-metallic complexes. During average years this may not represent an excessive stress to the plant. However, during droughts, trees with fine roots restricted to the organic horizon (such as at Site II) would be more severely stressed than trees physiologically acclimated to growing in humus over bedrock (such as at Site I). The observed alterations in tree growth at Site II may therefore be explained as a result of Al^{3+} toxicity and drought, whereas those at Site I may be due to drought alone or a combination of drought and other direct or indirect mechanisms.

Chronic vs Episodic Stress

Some of the most recent discussions of tree dieback and decline have dealt with whether this phenomenon is a result of chronic low-level stress or an episodic event, or a combination of the two (Johnson and Siccama 1983; Tomlinson 1983). Johnson and Siccama's (1983) results suggest that the drought of the 1960s may have triggered the red spruce decline in the northeastern United States and a drought in 1957 may have initiated the decline of conifers in southern New Jersey. The fact that these trees had recovered from earlier droughts may indicate that an episodic event, in this case drought, triggered dieback in trees predisposed by chronic low-level stress.

Tomlinson's (1983) paper was based largely on the European experience with forest decline as related to sulfur emissions and acid deposition effects. He contends that many of the effects now visible at remote sites are similar, if not identical, to those previously reported near smelters and other emission sources. Within the context of Tomlinson's hypothesis, the degree of forest decline is an expression of both the length of exposure to, and concentration of, air pollutants and acid deposition.

Although there have been numerous investigations of the effects of smelter and other point-source emissions on tree growth, only Thompson (1981) has used an approach similar to the one used in this investigation. Her case study of single-needle pinyon pine (*Pinus monophylla* Torr. & Frem.) involved comparison of response-function analyses of growth indexes from trees growing near a smelter in McGill, Nevada, and trees growing outside the area impacted by the smelter plume. The percent variance explained by climate was 83.5% for trees outside the impacted area, and 53.0% for trees inside the impacted area. Also, the percent variance explained by prior growth increased from 0.0% for unimpacted trees to 18.8% for impacted trees. The similarity of these results to those reported for the Hubbard Brook red spruce suggests that air pollution stress may have been involved in the decreased importance of climate and the increased importance of prior growth for both studies. As with the Hubbard Brook red spruce trees there were no visible signs of dieback or decline in the pinyon pine. This further suggests that visibly healthy trees may be enduring sublethal levels of physiological stress, which may be manifest as dieback when a triggering mechanism or level of stress occurs.

CONCLUSIONS

Forest dieback and decline are extremely controversial yet important issues. Although there is little direct evidence of the cause of these phenomena, there is considerable circumstantial evidence of a link to anthropogenic emissions. Acid deposition and air pollution may represent a chronic low-level stress which, when combined with high-stress events such as extreme drought, result in synchronous, region-wide tree dieback and decline. Because of the circumstantial nature of the evidence currently available, caution must be taken in interpreting those data. This is particularly important because most of our eastern forests are only now reaching maturity following widespread timber harvesting around the turn of the 20th century. The impacts of such changes in land use are only now being considered.

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Alteration of Precipitation Chemistry by Deciduous and Coniferous Canopies

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ABSTRACT

Throughfall was collected in adjacent coniferous and deciduous stands in the Mill Run watershed in northwestern Virginia. Nine sample sets during a period of 13 weeks between July and November 1982 had mean pH values of 4.40, 4.37, and 4.11 for precipitation, deciduous throughfall, and coniferous throughfall, respectively. The pH of coniferous throughfall differed significantly ($P < 0.05$) from that of precipitation and deciduous throughfall. Beneath both canopy types there was a net gain of H^+, Ca^{2+}, Mg^{2+}, K^+, NO_3, and SO_4^{2-} and a net loss of NH_4^+. Calcium ions and Mg^{2+} were preferentially leached from conifers and K^+ from hardwoods. It is assumed that cations are leached from plant tissues at accelerated rates by H^+ exchange reactions, and by diffusion and mass flow.

INTRODUCTION

Although the capacity of forest canopies to alter the chemistry of precipitation has been recognized for some time, recent concern over the effects of acidic deposition has led to intensified research in this area. Enrichment of throughfall occurs by leaching ions from plant tissues and by washoff of dry-deposited elements. Cations are believed to be leached from plant tissues by exchange reactions involving H^+ in acid precipitation and by diffusion and mass flow through leaf surfaces (Tukey 1980). In temperate coniferous and deciduous forests impacted by wet and dry acidic deposition, the potential exists for accelerated leaching of nutrient ions from the canopy. The literature suggests that this is particularly true for cations such as Ca^{2+}, Mg^{2+}, and K^+. Leaching of ions from plant tissues by acid deposition may accelerate the rate of nutrient cycling, and therefore may place added stress on plants to replace the loss of leached ions.

Preliminary results from a research site in northwestern Virginia are examined with respect to the throughfall enrichment phenomenon. The relationship of relative throughfall enrichment by canopy type is also discussed.

MATERIALS AND METHODS

Study Area

Precipitation samples for this study were collected in the Mill Run watershed near Front Royal, Virginia, at latitude 38° 52′ N and longitude 78° 22′ W (Fig. 1). The watershed is in one of the driest parts of Virginia with average annual precipitation of 860 mm. Woody vegetation is dominated by mixed stands of scarlet oak (*Quercus coccinea* Muenchh.), chestnut oak (*Q. prinus* L.), and white oak (*Q. alba* L.), but also includes black gum (*Nyssa sylvatica* Marsh.), red maple (*Acer rubrum* L.), and hickory (*Carya* sp.). White pine (*Pinus strobus* L.), shortleaf pine (*P. echinata* Mill.), pitch pine (*P. rigida* Mill.), and Virginia pine (*P. virginiana* Mill.) were noted as scattered individuals and isolated stands. Tree ages established by ring counts of increment cores indicate that the forest has not been harvested since about 1880.

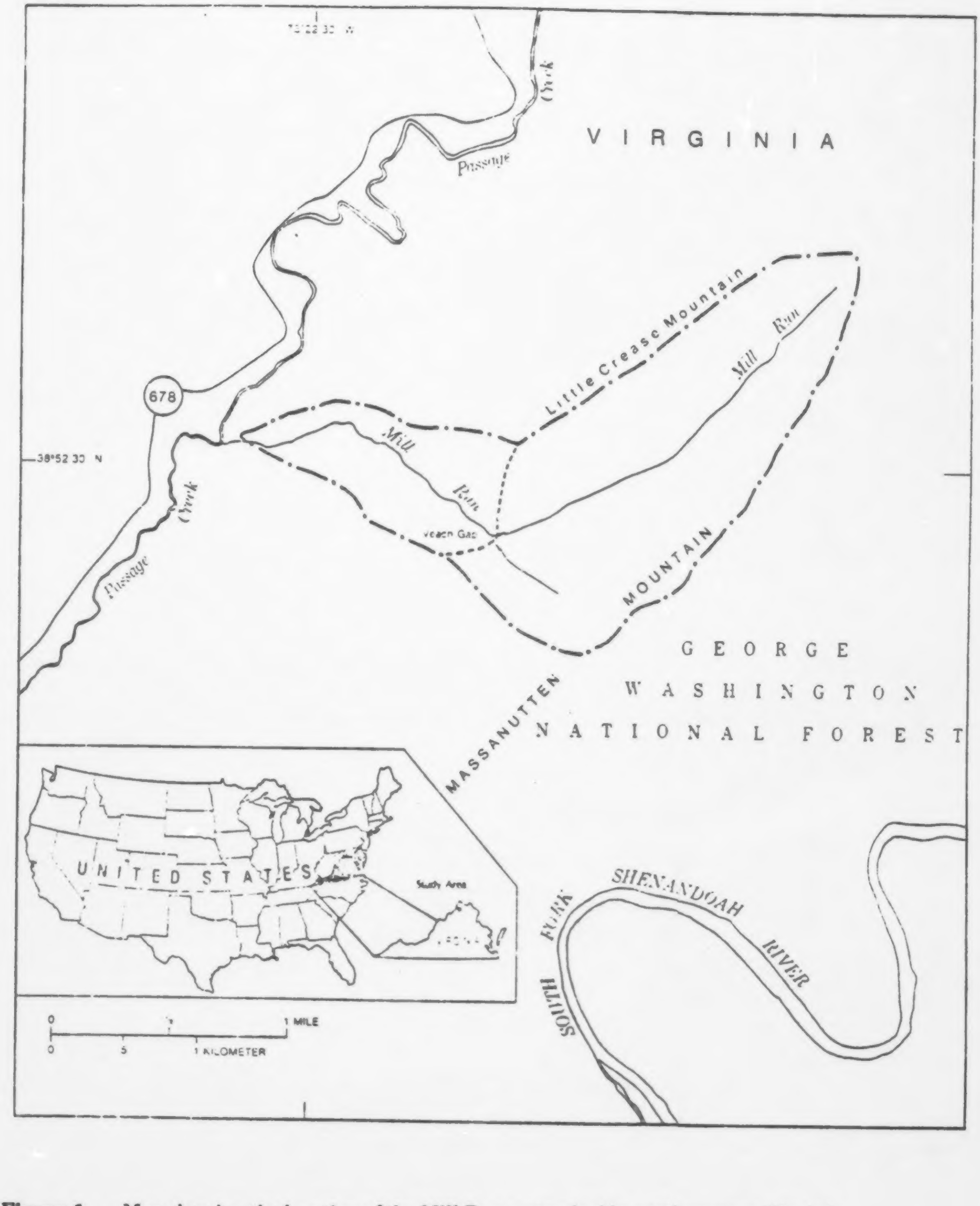
78°22'30" W
VIRGINIA
Passage Creek
Little Crease Mountain
Mill Run
678
38°52'30" N
Mill Run
Veach Gap
Passage Creek
MOUNTAIN
GEORGE WASHINGTON NATIONAL FOREST
MASSANUTTEN
UNITED STATES
Study Area
VIRGINIA
SOUTH FORK SHENANDOAH RIVER
0 1/2 1 MILE
0 .5 1 KILOMETER

Figure 1. Map showing the location of the Mill Run watershed in northwestern Virginia.

Methods

Collection of incident precipitation began in July 1982 in an open field adjacent to the watershed. Samples were collected in an Aerochem Metric model 301 automatic sampler[1] of the type used by the National Trends Network and the National Atmospheric Deposition Program. The quantity of precipitation was measured with Belfort weight-recording rain gauges. Throughfall was collected in adjacent deciduous and coniferous stands in paired automatic samplers of the Aerochem Metric design. The deciduous stand was composed of white oak, scarlet oak, black gum, red maple, and chestnut oak. The coniferous stand was mostly white pine, although shortleaf pine, pitch pine, Virginia pine, and scarlet oak were present but not directly over the collectors.

Samples were collected on a weekly basis and filtered in the field through Nucleopore 0.45- µm filters. A separate sample for metal analyses was acidified with Ultrex grade nitric acid. Electrometric measurements of pH and conductivity were made in the field and on occasion rechecked in the laboratory. Calcium and magnesium concentrations were measured from aliquots of acidified samples by atomic absorption spectrophotometry. Concentrations in microequivalents per litre of the ions Na^+, NH_4^+, K^+, Cl^-, NO_2^-, PO_4^{3-}, NO_3^-, and SO_4^{2-} were determined by ion chromatography. The quantity of precipitation was then multiplied by the ion concentrations to provide a quantitative measure of the total ion deposition per square decimetre during that sample period.

Net enrichment of throughfall was calculated by subtracting the ion concentration in precipitation from the corresponding throughfall concentration. In addition, relative enrichment was calculated as the difference between the respective coniferous and deciduous throughfall concentrations.

RESULTS AND DISCUSSION

The volume-weighted mean pH values during the July to November, 1982, sample period were 4.40, 4.37, and 4.11 respectively for precipitation, deciduous throughfall, and coniferous throughfall. The pH of coniferous throughfall differed significantly ($P < 0.05$) from that of precipitation and deciduous throughfall. Beneath both canopy types, there was a net enrichment of H^+, Ca^{2+}, Mg^{2+}, and K^+, and a net loss of NH_4^+ (Table 1). There was a net gain of Na^+ under conifers and a net loss under hardwoods. Hydrogen ion concentrations in incident precipitation, deciduous throughfall, and coniferous throughfall are given in Table 2.

Net cation enrichment of coniferous throughfall was dominated by Ca^{2+} (121.3 eq ha^{-1}), followed by H^+ (68.8 eq ha^{-1}), Mg^{2+} (42.2 eq ha^{-1}), and K^+ (39.4 eq ha^{-1}). Under the deciduous canopy, net cation enrichment of throughfall was primarily from Ca^{2+} (67.6 eq ha^{-1}), and K^+ (66.3 eq ha^{-1}) and to a lesser degree from Mg^{2+} (25.1 eq ha^{-1}). Net changes in the concentration of Na^+ (Table 1) are variable and probably are not different from those of precipitation. Throughfall under both canopy types exhibited a net loss of NH_4^+: 17.3 eq ha^{-1} under conifers and 24.7 eq ha^{-1} under hardwoods. Relative enrichment of cations was mainly from H^+ (63.1 eq ha^{-1}), Ca^{2+} (53.7 eq ha^{-1}), Mg^{2+} (17.1 eq ha^{-1}), and K^+ (26.9 eq ha^{-1}).

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[1] The use of trade, firm, or corporation names in this paper is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of the Interior or the Geological Survey of any product or service to the exclusion of others that may be suitable.

Table 1. Total concentrations of ions (equivalents per hectare) in incident precipitation (Precip), coniferous throughfall (Conifer), net coniferous throughfall enrichment (C-P), deciduous throughfall (Decid), net deciduous throughfall enrichment (D-P), and relative enrichment (C-D)

	Precip	Conifer	C-P	Decid	D-P	C-D
H	72.6	141.4	68.8	78.3	5.7	63.1
Ca	17.2	138.5	121.3	84.8	67.6	53.7
Mg	0.1	42.3	42.2	25.2	25.1	17.1
Na	13.3	18.7	5.4	11.2	-2.1	7.5
NH_4	37.6	20.3	-17.3	12.9	-24.7	7.4
K	13.2	52.6	39.4	79.5	66.3	-26.9
Cl	44.0	47.6	3.6	38.6	-5.4	9.0
NO_2	0.2	0.4	0.2	2.5	2.3	-2.1
PO_4	1.8	0.6	-1.2	1.9	0.1	-1.3
NO_3	38.0	117.3	79.3	57.4	19.4	59.9
SO_4	94.6	223.2	128.6	175.6	81.0	47.6

Table 2. Hydrogen ion concentration (microequivalents per litre) ranges in incident precipitation, deciduous throughfall, and coniferous throughfall. pH values are in parentheses

	Minimum	Maximum
Incident precipitation	1.8 (5.74)	170.0 (3.77)
Deciduous throughfall	2.1 (5.67)	195.0 (3.71)
Coniferous throughfall	29.5 (4.53)	275.4 (3.56)

In precipitation and throughfall, the concentrations of the anions NO_2^- and PO_4^{3-} were nearly negligible (Table 1). Incident precipitation contained almost equal amounts of Cl^- (44.0 eq ha^{-1}) and NO_3^- (38.0 eq ha^{-1}), and the concentration of SO_4^{2-} (94.6 eq ha^{-1}) was nearly twice as large. Under hardwoods there was a net gain of 19.4 eq ha^{-1} NO_3^- and 81.0 eq ha^{-1} SO_4^{2-}. In coniferous throughfall there was a net gain of 79.3 eq ha^{-1} NO and 128.6 eq ha^{-1} SO_4^{2-}. Relative enrichment of anions was primarily from NO_3^- (59.9 eq ha^{-1}) and SO_4^{2-} (47.6 eq ha^{-1}).

Net enrichment of throughfall in relation to acidic deposition has been reported by several investigators (Eaton et al. 1973; Baker et al. 1976; Bache 1977; Cole and Johnson 1977; Lakhani and Miller 1980; Mayer and Ulrich 1980; Mollitor and Berg 1980; Parker et al. 1980). In addition, Tukey (1970, 1980) has provided excellent reviews of the leaching of substances from plants. The preliminary results of this investigation seem consistent with those reported in the literature.

Significant quantities of NO_3^-, SO_4^{2-}, and H^+ enter ecosystems in throughfall, much of it from dry deposition of gaseous and particulate nitrogen and sulfur (Garland and Branson 1977; Parker et al. 1980; Lovett and Lindberg 1983; Ulrich 1983). The excess H^+ may be added as nitric and sulfuric acid aerosols and gases which are adsorbed onto and/or enter the leaf itself (Nicholson and Peterson 1983). The net loss of NH_4^+ may also account for some of the H^+ flux. Miller and Miller (1983) reported a net gain of H^+ due to foliar uptake of NH_4^+ by nitrogen-deficient trees. They contend that uptake of NH_4^+ by the forest canopy necessitates a reciprocal H^+ flux. It is also possible for sulfur and nitrogen oxides to enter leaves through the stomata or to be adsorbed onto the wet surfaces of plant tissues (Ulrich 1983). Further oxidation and hydrolysis of these oxides may result in the formation of H_2SO_4 and HNO_3. Parker et al. (1980) have suggested that as much as 50 to 70% of the SO_4^{2-} in net throughfall may result from dry deposition. Some of the enrichment may also be due to removal of excess SO_4^{2-} from the leaf itself as part of the internal cycling process. However, this same process seems unlikely for NO_3^-. Although SO_4^{2-} accumulates in conifers (and also presumably in hardwoods) if there is an excess of sulfur, nitrogen rarely exists in leaves of forest trees in an inorganic form (Lambert and Turner 1977). This is evident in recent research by Lovett and Lindberg (1983) which suggests that 100% of NO_3^- in net throughfall is from dry deposition of gaseous HNO_3 and particulate NO_3^-.

In this study, Ca^{2+}, Mg^{2+}, and K^+ were leached in considerable quantities from both coniferous and deciduous canopies. Tukey (1980) maintains that cations are leached from exchangeable cation pools in free spaces in plant tissues. He further adds that cations may be leached from exchange sites by hydrogen ions in the leaching solution and/or by diffusion and mass flow from the translocation stream to the leaching solution. Ulrich (1983) has proposed that cations may be leached from the stomatal cavity by H_2SO_4 and HNO_3 aerosols and gases entering through the stomata. As discussed above these acids may also be formed in situ from gaseous sulfur and nitrogen oxides taken in through stomata.

From the viewpoint of relative enrichment, Ca^{2+} and Mg^{2+} were leached to a greater degree from conifers, whereas K^+ removal was greater under hardwood canopies. This is not too surprising in light of the fact that Ca^{2+} and Mg^{2+} uptake by coniferous and deciduous species may exceed the annual requirements for growth (Cole and Rapp 1981). Also calcium uptake by conifers has been shown to be more than double that of deciduous species (Cole and Rapp 1981). Potassium, however, is more mobile in hardwoods (Eaton et al. 1973; Mollitor and Berg 1980; Cole and Rapp 1981) which might account for the greater net enrichment under the deciduous canopy. One interesting difference between coniferous and deciduous net throughfall with respect to relative enrichment (Table 1) is the balance between the sum of H^+ and Ca^{2+} (116.8 eq ha^{-1}) and the sum of NO_3^- and SO_4^{2-} (107.5 eq ha^{-1}). This suggests that, at least in conifers, leaching of Ca^{2+} from plant tissues buffers some of the H^+ acidity which enters the canopy through wet and dry deposition of H_2SO_4 and HNO_3.

Because Ca^{2+} and Mg^{2+} are taken up in greater quantities than required by both conifers and hardwoods (Cole and Rapp 1981), it is difficult to ascertain if the accelerated leaching rates are a potential added stress. It seems more likely that K^+ leaching represents a greater stress in view of the lower rate of uptake and its reported role in the regulation of stomatal function (Meyer et al. 1973). Rehfuess et al. (1982) reported Ca and Mg deficiencies in unhealthy conifers compared to healthy trees growing in southern Germany, which they attributed to accelerated leaching from plant tissues by acid deposition. Potassium deficiency was not apparent, possibly because the soils in that region are rich in potassium. Whether or not leaching of cations results in added stress may depend largely on the ability of the plant to replace the cations and on their availability in the soil nutrient pool.

Incident precipitation falling through forest canopies becomes enriched in both cations (H^+, Ca^{2+}, Mg^{2+}, K^+) and anions (NO_3^-, SO_4^{2-}). Leaching of Ca^{2+}, Mg^{2+}, and K^+ from plant tissues may account for most of the net throughfall enrichment of these ions. Dry deposition processes are considered to be the major source of net throughfall enrichment for NO_3^- and SO_4^{2-}. Net gains of H^+ are assumed to be associated with dry deposition of HNO_3 and H_2SO_4. However, at the present time, there is no direct evidence, either in this investigation or in the literature, on which to base precise estimates of the relative importance of dry-deposited and internally cycled nutrients in enrichment of precipitation by forest canopies.

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Incident Rain Characterization

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ABSTRACT

Cluster analysis was used to determine if the quantity of rainfall in a rain event had an influence on the chemical composition of incident rain sampled in bulk collectors. The parameters used in the analysis were quantity of rain and volume-weighted concentrations (μeq L^{-1}) of H, NO_3, SO_4, Ca and Na. Eighteen rain events from a remote site 80 km north of Québec City were clustered to cover a period from May 5, 1981, to October 10, 1981. Six groups were identified. The quantity of rain that had fallen did not seem to affect the quality of the rain. Small and large rain events may both have lower and higher pHs. The sequence of the classification of the six groups followed a temporal sequence from spring to fall. Four groups in May identified four separate events, a fifth group identified four rain events in June and a sixth group identified 10 events from July to October. These groupings indicated extreme variability between rain events in the spring and more homogeneous events in the summer and fall periods. In the four spring groups rain pH decreased from 4.37 in mid-spring to 3.88 in late spring (a period of 13 days). This increase in acidity from pH 4.33 to 4.06 to 3.88 corresponded to a decrease in Ca from 6.8 to 0.2 to 0 μeq L^{-1} and to a concomitant increase in NO_3 and SO_4 from 0.9 to 1.3 to 3.5 μeq L^{-1} and from 23 to 34 to 68 μeq L^{-1} respectively. The low levels of NO_3 and SO_4 may account for the pH of 4.37 in the absence of Ca. In small rainfalls the amount of NO_3 and SO_4 may control rain pH. The lower the SO_4:NO_3 ratio the lower the pH, indicating the importance of NO_3 in these rain events, Ca being absent. Larger rainfalls with low Ca values also follow this pattern.

Spatial Variations in the Precipitation Chemistry in a Boreal Forest

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ABSTRACT

From June to October 1982, incident rain, throughfall and stemflow were sampled on a weekly basis in a balsam fir-white birch forest, 80 km north of Québec City in the Laurentide Reserve. Eighty percent of the forest was composed of balsam fir. The average volume-weighted pH values for 13 samples were 4.40, 4.40 and 4.14 for incident rain, throughfall and stemflow respectively. Anions dominated the incident rain while a surplus of base cations was found in the throughfall and stemflow, as indicated by the sum cation:sum anion ratios of 0.8, 1.1 and 1.1 respectively. For the cations K, Ca, Mg, Na and NH_4 increased concentrations were found in both throughfall and stemflow. The H concentration increased only in the stemflow by an enrichment factor of 1.8. For the anions PO_4, SO_4 and Cl, enrichment was measured in both throughfall and stemflow. NO_3, on the other hand, was absorbed by the canopy as the rain passed through it. A decreased Ca:Mg ratio to 2.33 and 3.02 and an increased K:Na ratio to 1.52 and 9.17 in both throughfall and stemflow seemed to indicate a preferential leaching of Mg and K from the vegetation. Hydrogen made up 30% of the total ionic charge in the incident rain. This decreased to 19% and 10% respectively in throughfall and stemflow. Ca and Mg summed to 6% of the total ionic charge in the incident rain with an increase to 17% and 20% in the throughfall and stemflow. Nitrate made up less than 1 % of the charge in the latter. Dry deposition did not seem to be an important factor as shown by a decreased contribution of SO_4 to the total ionic charge of the infiltrating precipitation.

Chemical Effects of Simulated Acid Rain on Two Forest Soils

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ABSTRACT

Parallel laboratory and field experiments were conducted in which soil columns from the Turkey Lake and Montmorency Forest watersheds were watered with simulated rainfall of pH 5.7, 3.5, and 2. The watering solutions had been acidified with dilute H_2SO_4/HNO_3 in a ratio of 2.5:1. Soil pore water samples were analyzed for H^+, NH_4^+, Na, K, Ca, Mg, Fe, Mn, Al, SO_4^{2-}, NO_3^-, and Cl^-. Following treatment, a number of soil properties were themselves studied. Accelerated leaching of cations, especially Ca and Al (and NH_4^+ in the laboratory columns) was observed as a result of pH 2 acid treatment; SO_4^{2-} was the principal anion carrier. Deposition of SO_4^{2-} was most prominent in the litter-humus layer and in the region of the Bfh horizon. The highly acidic treatment led to significant replacement of metallic cations by hydrogen on the exchange complex, and there is tentative evidence of accelerated podzolization under these conditions. There were smaller changes in cation content of pore water when watering was done with pH 3.5 compared with pH 5.7 rainfall.

INTRODUCTION

In order to understand better the possible effects of acid rain on important soils of the Canadian Shield in central Canada, an experiment was undertaken wherein reconstructed soil columns were watered with simulated rainfall of three different pH values. After watering over a 365-day period, with the addition of 1070 mm of rainfall to each column, the columns were dismantled and some of the important soil properties measured. This experiment, along with parallel field experiments and accelerated leaching studies, is described in detail elsewhere (vanLoon and Rutherford 1983). This paper summarizes some of the data obtained with respect to cation exchange capacity, base saturation, movement of iron and aluminum in the soil, and the effects of the sesquioxides on the retention of sulfate by the soil.

EXPERIMENTAL

The Soil Columns

Soil samples were obtained from areas currently operated by the Canadian Forestry Service as part of their research project on the effects of acid precipitation on the forest ecosystem. These are located at the Turkey Lake Watershed near Sault Ste. Marie, Ontario, an area of mixed hardwood forest on a brunisolic soil, and at the Montmorency Forest about 120 km north of Quebec City. The latter is an area of boreal balsam fir forest with podzolic soils.

Undisturbed cores consisting of the top 17 cm of soil were taken using a steel sampler with the same internal diameter as the laboratory columns themselves. These cores generally were made up of L, H, and Ae horizon material. Soil below the undisturbed cores was obtained by sampling layers in the field. Beginning at a depth of 17 cm, samples of 2.5, 2.5, 2.5, 2.5, 2.5, 12.5, and 15 cm were taken from a pit adjacent to the core sampling site. These samples were dried and passed through a 2-mm seive.

The laboratory columns were constructed of 6.4-mm-thick polymethylmethacrylate plastic cylinders with 15.4 cm internal diameter and a length of 63 cm. They were filled with soil, beginning at the top with the undisturbed core and then layer by layer so as to reconstruct the original horizonation. Plates of the same plastic material were solvent-welded to the base of each column after filling. Drainage was facilitated by a 2-cm layer of polyethylene beads on which a heavy nylon ballistic fabric sieve had been placed, at the bottom of each column. Eighteen columns of each soil type were prepared.

Provision was made for obtaining samples of pore water at depths of 12, 25, and 60 cm.

Watering

The soils were watered with three types of simulated rainfall: pH 5.7 (deionized, distilled water), pH 3.5 (125 µM H_2SO_4 + 65 µM HNO_3), and pH 2.0 (4 mM H_2SO_4 + 2 mM HNO_3). Six replicates of each treatment were given. Each column was watered every week with 20 mm (360 mL) of the appropriate rainfall by means of a perforated tray which ensured slow, even distribution. After 249 days, the columns were subjected to a freeze-thaw process to simulate the winter season. Polyethylene sheet discs were placed on the soil surface of each column and the top 40 cm were surrounded with fibreglass insulation. Dry ice was then placed on the polyethylene discs. During the 12 to 14 hours required for the dry ice to sublime, the top 3 cm (approximately) of the soil froze. After this treatment, a larger flux of rainfall (50 mm) was passed through each column, simulating the percolating waters of spring runoff.

Recovering Soil Samples for Analysis

After 365 days, three of the six columns undergoing each treatment were dismantled, and the soil extruded and collected in layers according to the observed pattern of horizons. Seven to nine samples were obtained from each column.

Analysis of Soils

Exchange cations, titratable acidity, cation exchange capacity, and base saturation were determined by method 5 in the paper by Nommik (1974). Iron and aluminum concentrations were determined using three different extracting solutions based on dithionite, oxalate, and pyrophosphate (Wang 1978).

RESULTS

Mean values of the cation exchange capacity (CEC) and base saturation for approximately equivalent horizons and depths in the two soils are given in Table 1.

At Montmorency, the CEC in the litter-humus layer appears to have been significantly reduced after treatment with pH 2 rainfall. Furthermore, the already-low base saturation in the mineral soil was somewhat less in all horizons after this treatment. A smaller decrease in base saturation appears to have occurred after the pH 3.5 treatment.

Table 1. Cation exchange capacity (meq 100 g^{-1}) and base saturation (%) of soils before and after treatment in the long columns. Values are means of three columns

Approx. depth of horizon (cm)	Before	After treatment pH 5.7	 pH 3.5	 pH 2.0
Montmorency				
LH	27.5 (90)	20.7 (59)	21.0 (58)	15.2 (24)
Ae	1.3 (34)	1.5 (28)	2.9 (26)	1.5 (27)
15 - 20	4.1 (17)	3.7 (12)	4.3 (10)	2.7 (10)
20 - 30	3.8 (11)	3.9 (12)	3.8 (10)	4.1 (6)
30 - 45	3.7 (14)	3.5 (15)	3.5 (13)	3.8 (10)
> 45	2.2 (22)	2.5 (22)	2.9 (18)	3.1 (18)
Sault Ste. Marie				
LH	29.9 (88)	14.6 (76)	15.9 (79)	11.8 (43)
Ae (usually indistinct)	5.8 (50)	6.5 (35)	4.8 (48)	5.1 (11)
15 - 20	4.8 (43)	5.2 (18)	4.6 (32)	4.9 (13)
20 - 30	3.3 (33)	4.1 (21)	3.2 (28)	3.0 (36)
30 - 45	1.9 (30)	2.6 (26)	1.7 (35)	1.8 (50)
> 45	0.6 (61)	1.3 (37)	0.9 (51)	1.1 (49)

At Sault Ste. Marie (SSM) there is more variation in the results. This is partly a consequence of the large differences in organic carbon content in the upper layer of this soil. The CEC in the litter-humus layer was also lower after pH 2 treatment, as was the base saturation down to a depth of 20 cm. Surprisingly, however, the base saturation at all depths after pH 3.5 treatment was higher than after pH 5.7 treatment, although the CEC was lower. Furthermore, base saturation of samples taken from the pH 2 columns was also higher for soils at depths greater than 20 cm.

While the reduction in base saturation is predictable, the decrease in CEC in the LH layer is perhaps more surprising. This is not due to a loss of organic material in total from that part of the soil. The mean total organic carbon contents in the LH layer after all treatments at both sites are comparable. Furthermore, additional experiments have shown that significantly more total carbon was leached from soils by pH 5.7 rain than by more acidic rain. It may be that accelerated leaching of certain classes of organic compounds responsible for cation exchange did occur at low pH. For example, high levels of amino nitrogen were detected in the effluent solutions under these conditions.

Iron and Aluminum Oxides

Tables 2 to 5 show results obtained from iron and aluminum fractionation studies on the soils from the long laboratory columns. The methods recommended by Wang (1978) were used in these studies. These estimated quantities of crystalline, inorganic amorphous, and organic amorphous iron oxides, as well as inorganic amorphous and organic amorphous aluminum oxides in the soil at various depths after treatment. These procedures do not provide a clear-cut separation, but give a reasonable indication of the amounts of the different forms. A simplified explanation of the method is that the pyrophosphate solution extracts organically-bound Fe and Al from the soil. Ammonium oxalate solution extracts this fraction plus amorphous inorganic oxides of both Fe and Al. Dithionite solution removes both the above forms of Fe as well as crystalline Fe oxides. Dithionite, a reductant, has not been recommended as an extractant for Al in the soil. In addition to not providing a completely clear separation, this method is subject to some specific anomalies. The best known of these is that crystalline olivine and magnetite are substantially insoluble in ammonium oxalate, but have limited solubility in dithionite solution. It thus becomes possible to obtain higher Fe results in oxalate rather than dithionite solutions in specific instances.

Table 2. Fe speciation at various depths (%) (Montmorency)

		Column number								
		pH 5.7			pH 3.5			pH 2.0		
		1	2	6	13	14	18	25	26	30
	x	0.0	0.0	0.0	0.08	0.0	0.0	0.0	0.0	0.0
LH	a	0.46	0.17	0.24	0.29	0.29	0.35	0.31	0.33	0.48
	or	0.51	0.18	0.18	0.21	0.29	0.36	0.28	0.43	0.30
	x	0.09	0.05	0.0	0.03	0.0	0.0	0.0	0.02	0.08
Ae	a	0.04	0.01	0.13	0.22	0.12	0.0	0.08	0.07	0.0
	or	0.10	0.09	0.10	0.20	0.19	0.06	0.14	0.11	0.02
	x	0.0	0.0	0.0	-	0.0	0.0	0.0	0.0	0.18
15-20	a	0.96	0.84	1.14	-	0.87	0.84	0.51	0.38	0.54
	or	0.89	0.91	1.26	1.55	1.25	0.82	0.51	0.41	0.74
	x	0.0	-	0.0	-	0.0	0.0	0.0	0.0	0.0
20-30	a	1.46	1.37	1.14	-	1.13	1.01	0.88	1.11	0.84
	or	1.43	1.41	1.64	-	1.60	1.29	1.20	1.39	1.09
	x	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30-45	a	1.57	1.45	1.59	1.22	1.17	1.00	1.04	1.40	1.15
	or	1.64	1.74	1.43	1.91	1.64	1.91	1.83	1.55	1.43
	x	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.06
> 45	a	2.13	1.78	1.93	1.20	1.25	1.21	1.20	1.28	1.27
	or	1.13	1.06	1.05	1.20	1.05	1.25	1.25	1.06	1.64

x crystalline sesquioxides, Fe_d-Fe_o (values of 0 are usually slightly negative
a amorphous sesquioxides, Fe_o-Fe_p
or organically bound sesquioxides, Fe_p

Both Montmorency and SSM soils indicate a region of low Fe and Al values at about 10-15 cm just below the organic layer (identified as Ae horizon). This was visually much more distinct at Montmorency and the Fe results were generally lower there. Some of the SSM cores had no visible Ae horizon. For these samples, chemical analyses also indicated high Fe and Al values comparable to adjacent portions of the mineral soil. Immediately below the Ae horizon occurred a darker zone where both Fe and Al values (amorphous inorganic and amorphous organic metal to be specific) were high. In all samples analyzed the sum of Fe_p and Al_p was always greater than 0.6%, thus meeting one of the key criteria for identifying this as a B_f horizon.

Table 3. Al speciation at various depths (%) (Sault Ste. Marie)

		Column number								
		pH 5.7			pH 3.5			pH 2.0		
		7	11	12	19	23	24	31	35	36
LH	a	0.15	0.0	0.13	0.0	0.0	0.0	0.0	0.11	0.0
	or	0.54	0.31	0.18	0.25	0.33	0.33	0.14	0.16	0.12
Ae	a	-	0.0	-	0.0	0.0	0.0	0.0	-	0.0
	or	-	0.16	-	0.34	0.08	0.31	0.10	-	0.10
15-20	a	1.60	0.02	0.58	0.23	0.0	0.60	0.51	0.17	0.03
	or	1.97	1.41	1.05	1.47	1.03	1.48	1.53	0.93	0.91
20-30	a	0.99	0.09	0.54	0.07	0.40	0.67	0.93	0.57	0.56
	or	1.72	1.95	1.54	1.46	1.52	1.64	1.46	1.39	1.24
30-45	a	0.40	0.42	0.65	0.47	0.57	0.37	0.96	0.37	0.96
	or	1.56	1.44	1.31	1.31	1.39	1.67	1.16	1.08	0.57
> 45	a	0.46	0.16	0.62	0.46	0.56	0.56	0.65	0.65	0.69
	or	0.64	0.62	0.60	0.56	0.62	0.54	0.53	0.64	0.49

a amorphous sesquioxides, Al_o-Al_p
or organically bound sesquioxides, Al_p

In most of the samples studied the amount of crystalline Fe oxides, as calculated from Fe_d-Fe_o, was small, and, in fact, at Montmorency the majority of these values were negative. Data from the same area reported by Robitaille (1983) also indicate very low (but usually positive) Fe_d-Fe_o values.

Comparable amounts of amorphous inorganic and organic Fe were found in both the soils. The ratio Fe_a/Fe_{or} increased with depth from the B_{fj} horizon downward at SSM but there was no clear trend at Montmorency. In contrast to Fe, a greater proportion of Al was identified with the organic fraction and the ratio of Al_a/Al_{or} again decreased with depth at SSM.

The results were also examined in order to note any soil changes due to the various treatments. There is considerable variability in individual results and it is not possible to observe any significant differences between the pH 5.7 and 3.5 treatments. In the Montmorency soil, the pH 2.0 treatment did show that Fe_a, or Fe_{or} and (less clearly) Al_{or} values were lower than for the other treatments in the region of 15-20 cm. There appears to be enhanced illuviation in this region as a result of the highly acidic input. This is corroborated by the visual observation of a much deepened light-coloured Ae layer in the columns after these treatments.

Table 4. Fe speciation at various depths (%) (Sault Ste. Marie)

		Column number								
		pH 5.7			pH 3.5			pH 2.0		
		7	11	12	19	23	24	31	35	36
	x	0.0	0.18	0.14	-	0.27	0.37	0.27	0.15	0.35
LH	a	0.76	0.22	0.34	-	0.24	0.25	0.37	0.33	0.20
	or	1.24	0.20	0.62	0.33	0.42	0.56	0.60	0.42	0.35
	x	-	0.26	-	0.22	0.41	0.31	0.31	-	0.29
Ae	a	-	0.24	-	0.26	0.13	0.22	0.17	-	0.26
	or	-	0.35	-	0.48	0.02	0.40	0.30	-	0.29
	x	0.0	0.45	0.0	0.0	0.27	0.13	0.03	0.06	0.0
15-20	a	1.07	1.06	0.64	0.70	1.04	0.84	1.57	0.87	1.15
	or	1.44	2.00	0.59	0.94	1.96	1.01	2.20	1.19	1.65
	x	0.0	0.04	0.07	0.14	0.07	0.01	0.19	0.0	0.0
20-30	a	0.81	1.19	0.83	0.52	0.86	0.94	0.94	0.91	0.70
	or	0.84	1.65	1.09	0.78	1.09	1.19	0.95	0.70	0.51
	x	0.0	0.0	0.04	0.0	0.14	0.03	0.16	0.0	0.02
30-45	a	0.70	0.74	0.58	0.60	0.56	0.65	0.61	0.68	0.48
	or	0.91	0.85	0.44	0.60	0.53	0.44	0.51	0.44	0.19
	x	0.0	0.0	0.0	0.09	0.0	0.0	0.0	0.0	0.0
> 45	a	0.48	0.54	0.57	0.45	0.59	0.56	0.53	0.50	0.49
	or	0.26	0.21	0.17	0.17	0.16	0.17	0.20	0.20	0.17

x crystalline sesquioxides, Fe_d-Fe_o (values of 0 are usually slightly negative
a amorphous sesquioxides, Fe_o-Fe_p
or organically bound sesquioxides, Fe_p

Interestingly, no such effect was observed or measured in the Sault Ste. Marie columns even at pH 2.0. There is considerable variation in the nature of the SSM cores (vanLoon and Rutherford 1983), and this leads to greater variability in the results for Fe speciation. In addition to this, it does appear that this soil is more resistant to changes due to acidity than is the Montmorency soil since only minor differences in CEC and Fe and Al speciation were observed after the highly acidic treatment.

Increased downward mobility of Fe and Al as inorganic ions would be predicted with increased acidity of rainfall. However, the situation is complicated by the fact that these elements move in the soil solution in large part as organic complexes. Because organic material is less soluble under acidic conditions (vanLoon and Rutherford 1983), lower concentrations of organic Fe and Al would be mobilized by acid rainfall. Which of these two factors is predominant or whether there is an approximate balance depends on the soil, and it appears that these two soils respond differently.

Table 5. Al speciation at various depths (%) (Montmorency)

		Column number								
		pH 5.7			pH 3.5			pH 2.0		
		1	2	6	13	14	18	25	26	30
LH	a	0.12	0.0	0.33	0.0	0.0	0.0	0.0	0.01	0.0
	or	0.90	0.46	0.28	0.26	0.51	0.70	0.70	0.75	0.44
Ae	a	0.0	0.0	0.0	0.0	0.0	0.08	0.03	0.04	0.0
10-15	or	0.16	0.21	0.16	0.21	0.28	0.08	0.13	0.06	0.06
15-20	a	0.0	0.0	0.40	0.15	0.0	0.02	0.0	0.10	0.0
	or	0.59	0.70	1.05	0.66	0.77	0.41	0.31	0.25	0.49
20-30	a	0.0	-	0.37	0.05	0.04	0.04	0.04	0.0	0.22
	or	1.03	1.08	1.34	1.13	1.29	0.90	0.98	1.07	0.72
30-45	a	0.0	0.0	0.47	0.29	0.0	0.11	1.30	0.32	0.19
	or	1.70	1.89	1.53	1.59	1.69	1.67	1.52	1.64	1.50
> 45	a	0.0	0.86	0.71	0.39	0.0	0.0	0.57	0.49	0.30
	or	2.07	1.59	1.49	1.49	1.46	1.56	1.39	1.39	1.74

a amorphous sesquioxides, Al_o-Al_p
or organically bound sesquioxides, Al_p

In summary, at Montmorency accelerated illuviation occurred under highly acidic treatment, but little change was observed under the same conditions at Sault Ste. Marie.

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Cuticular and Dendrochronological Features as as Indicators of Environmental Pollution

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ABSTRACT

Several plant populations of red oak (*Quercus rubra*) and sweetgum (*Liquidambar styraciflua*) growing in habitats characterized by varied levels of environmental pollution were studied for dendrochronological and cuticular patterns. Growth rings, ring and porous wood, and related features were analyzed with a dendrochronograph. Cuticular patterns such as stomatal frequency, stomatal size, and trichome frequency and type were studied in relation to environmental pollution in various habitats. Most plant populations under investigation were in the industrial areas of Nashville, Tennessee, known for their high levels of environmental pollution. Statistical analysis of the data revealed the significance of plant features as indicators of environmental pollution in the area. Growth rings were extremely narrow in highly polluted areas, whereas the plant population exhibited fully developed annual increments in relatively low levels of environmental pollution. Trichome frequency increased with pollution, whereas stomatal frequency decreased in polluted habitats. Stomatal size was not significantly affected by different levels of pollution in the environment. In addition, certain morphological features showed adaptations to varied amounts of environmental pollution.

INTRODUCTION

In our highly industrialized world, it is important that we find and explore different methods of monitoring the air pollution found in our environment. Ecologists and environmentalists are continually looking for new methods of monitoring environmental pollution. Relatively new fields of environmental research, opened up in recent years, may also be used to monitor the pollution levels in the environment. These new fields are represented by dendrochronology, dendroecology, and cuticular patterns, as related to environmental pollution.

Dendrochronology is the science of dating annual layers (rings) in woody plants. Two related subdisciplines are dendroclimatology and dendroecology. The former uses the information in dated rings to study problems of present and past climates. The latter deals with changes in the local environment rather than regional climate (Fritts 1971).

Cuticular patterns have been used for taxonomic and paleobotanical studies. However, their utilization in the study of environmental problems is a fairly recent field of research.

Numerous studies have been conducted which reveal the significance of tree ring widths in relation to climatology. However, relatively little information is available on the relationship between environmental pollution and growth rings produced by trees. Some studies, however, do suggest a relationship between high levels of environmental pollution and reduced plant growth, premature defoliation, and reduced leaf growth.

Smith (1973) reported that, at high levels of pollution, plants may suffer damage expressed as reduced growth. This effect may be due to the fact that forests serve as sinks for ammonia, hydrogen fluoride, sulfur dioxide, and ozone. According to a study conducted by the U.S.D.A. Forest Service

(1974), air pollutants damage trees primarily through defoliation. This injury is generally thought to be more severe in conifers than in hardwoods. Fritts (1966) suggests that because climate influences needle growth of conifers, it can control the photosynthetic area produced in any one season. Studies by Sharma and Madsen (1978) suggest that for *Liquidambar styraciflua* (sweet gum) the bark does not show a significant variation in pH with an obvious change in the degree of environmental pollution. Bark color undergoes darker pigmentation in polluted areas. Cover by epiphytes decreases with increased pollution level. Bark thickness is not significantly affected by pollution, although a slight trend for thicker bark in polluted areas is indicated, perhaps an adaptive response to a polluted environment.

Hay (1971) found that chimney smoke from a large factory in Germany resulted in a significant decrease in the width of growth rings of 75-year-old pines which stood 900 yards from the factory.

A recent study (Thompson 1981) reveals the responses of growth rings of *Pinus monophylla* (single-needle pinyon pine) in Nevada to air pollution caused by copper-smelter effluent.

In addition, several studies (Solberg and Adams 1956; Sharma and Butler 1973; Sharma and Madsen 1978) show the relationships between environmental pollution and gross morphological features of plants. Furthermore, cuticular features of plant leaves are excellent indicators of environmental pollution. A study by Sharma and Tyree (1973) indicates the usefulness of cuticular patterns in studying the impact of environmental pollution on plants and, hence, their reliability as bioindicators of environmental pollution. In view of these ecological investigations, studies were made of the cuticular features of *Liquidambar styraciflua* (sweetgum) and dendrochronological features of *Quercus rubra* L. (red oak) in relation to environmental pollution. The resulting information suggested these woody plant species as bioindicators of environmental pollution, a relatively inexpensive way to study plant-pollution relationships.

Sweetgum (*Liquidambar styraciflua* L.) and *Quercus rubra* L. are two of the most important commercial hardwoods in the United States. Part of the woods' unusual value is the ability of its veneer to take finishes in imitation of more expensive woods such as mahogony or black walnut (Harlow and Harrar 1958).

MATERIALS AND METHODS

For dendrochronological-pollution studies, two plant populations consisting of 20 tree samples of *Quercus rubra* L. (red oak) were studied. Population A, consisting of 10 trees, was taken from the heavily polluted metropolitan area of Nashville, Tennessee, U.S.A. Population B was collected from the rural, less polluted community of Martin, Tennessee, approximately 80 km west of Nashville. No measurements of environmental pollution levels were made, although great care was taken to note the locale and diversity of the two microhabitats with respect to actual and potential sources of environmental pollutants. Both plant populations were collected from uniform terrain conditions, thus minimizing the overall variations in growth rings caused by microhabitat parameters, such as soil moisture and temperature.

Nashville, the capital of Tennessee, is located in the middle of the state. It is highly industrialized and is subject to environmental pollution from a variety of sources. Sulfur dioxide sources include a heating plant, textile plant, glass-manufacturing plant, and emissions from heavy traffic. Additional sources of pollution are a fertilizer plant and a busy commercial jet airport. Mathis and Tomlinson (1972) reported that Nashville ranks twentieth in sulfur dioxide levels among cities in the United States. Martin is located in a rural area of northwest Tennessee where environmental pollution is limited mainly to auto emissions, which are relatively small compared to the Nashville area (Table 1).

Table 1. Distribution of experimental populations of *Quercus rubra* L. of *Liquidambar styraciflua* L. in Tennessee, U.S.A.

Population	Locality	Relative degree of pollution	Source of pollution
A	Nashville	+ + + + + +	Heavy industry, automobiles
B	Martin	+	Automobiles

+ + + + + + highest degree; + lowest degree

Table 2. Summary of dendrochronological, cuticular, and vegetative characteristics in Quercus rubra L./Liquidambar styraciflua L. in Tennessee, U.S.A.

Feature	Population A	Population B
Annual ring width (mm), x ± σ *	3.14 ± 0.40	5.14 ± 0.63
Leaf length (cm), x ± σ	11.9 ± 1.7	14.4 ± 1.2
Leaf width (cm), x ± σ	16.9 ± 2.2	18.9 ± 2.2
Petiole length (cm), x ± σ	11.7 ± 3.1	13.4 ± 2.2
Stomatal frequency, lower surface, ** x ± σ	35.1 ± 2.6	41.1 ± 2.0
Stomatal size range (μ), x	46-56	46-61
Trichome density/unit area (0.152 mm^2), x	8	6

* x = mean; σ = standard deviation

** mean stomatal frequency = stomata observed through a 40x objective and 10x oculars

Forty core samples were extracted from 10 randomly selected trees in each population. The dbh (diameter breast height) of the trees sampled varied from 50 to 55 cm. Core samples were extracted with a Swedish increment borer and were then analyzed with a dendrochronograph. Statistical analysis of the dendrochronological data is shown in Table 2.

For cuticular-pollution studies, each plant population of sweetgum (*Liquidambar styraciflua* L.) consisted of 25 leaves collected at random from sweetgum trees, a species considered ideal for cuticular studies because of its taxonomic and commercial significance. The leaf samples were collected in autumn to ensure their maximum maturity at the time of sampling. In addition, gross morphological features were recorded and analyzed for the two populations (Table 2). Cuticular impressions of the upper and lower leaf surfaces were prepared by applying Duco^R cement to the washed and air-dried leaves (Williams 1973). A small portion from the central area of these leaf imprints was used to make cuticular slides for the adaxial and abaxial leaf surfaces of each population. Cuticular features of these two plant populations were studied by randomly selecting 25 fields (n = 25) from each microscope slide. The microscopic analysis was done by using a 40x objective and 10x oculars. Statistical analysis of the cuticular data is shown in Table 2.

RESULTS AND DISCUSSION

Results are summarized in Table 2. There appears to be a significant difference in the mean annual width (growth ring) from areas with relatively high pollution levels as compared to areas of relatively low pollution. The mean width of annual rings for red oak in Martin, Tennessee (the rural population), from 1950 to 1974 was 5.14 mm. The mean width of growth rings in the highly polluted population of Nashville was 3.14 mm for the same period. In both cases, the low standard deviation values suggest added significance to the mean values. It appears that this difference in the width of growth rings is because of the obvious difference in environmental pollution in the two populations. Higher levels of environmental pollution seem to produce narrower growth rings. It seems reasonable to assume that reduced growth due to pollutants such as ammonia, hydrogen fluoride, sulfur dioxide, and ozone would have a negative effect on the width of growth rings. It is also of considerable importance to take into account the reduced growth effect of premature defoliation and reduced leaf growth on photosynthesis and, hence, reduced growth of annual rings.

Morphological and cuticular results from *Liquidambar styraciflua* L. indicate a marked difference in the response of plants to the varying levels of pollution. Table 2 indicates that leaf length, leaf width, and petiole length decreased with an increase in the level of pollution, as evident in the heavily polluted area of Nashville. Average leaf length decreased from 14.4 cm to 11.9 cm; the leaf width was 18.9 cm in population B and 16.9 cm in the heavily polluted population A of Nashville. Petiole length was 11.7 cm in the Nashville area whereas the Martin population showed a value of 13.4 cm. Again, low standard deviation values confirm the significance of these data.

Stomatal density was low in the polluted area and trichome frequency high. These adaptations suggest that plants shut off excessive gaseous pollutants by having fewer stomata and combat the detrimental effects of gaseous pollutants and particulate matter by high trichome frequency. Trichomes insulate the photosynthetic leaf surface, trap the particulate matter, and maintain low foliar temperature. Hence, the trichomes temper the detrimental effects of metabolic reactions caused by environmental pollutants.

A combination of vegetative, cuticular, and dendrochronological studies on a wide variety of plant taxa would supplement these findings on the use of dendrochronological and cuticular features of plants as indicators of environmental pollution in habitats throughout the world. Similar studies conducted under controlled growth conditions would provide valuable information for the interpretation of ecological and environmental impact problems.

CONCLUSIONS

These investigations of cuticular and dendrochronological features of sweetgum and red oak respectively emphasize that most of these features respond to environmental pollution and hence can be used as excellent indicators of environmental contamination. Additional plant taxa must be investigated for a complete understanding of these plant-pollution relationships. This field of investigation is relatively new and seems promising for studies dealing with environmental problems.

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Potential Effects of Acid Precipitation on Forest Wildlife

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ABSTRACT

Wildlife species such as moose, deer, and caribou and many smaller but ecologically significant herbivores live in forested areas of eastern North America receiving acidic precipitation. Based on a literature review we suggest that these herbivores may be affected indirectly by acid precipitation through changes in their forages and habitat. Acidification of soil-plant systems may reduce plant diversity, increase foliar concentrations of some heavy metals and decrease foliar concentrations of nutrients essential to herbivore nutrition.

The Canadian Wildlife Service is conducting research on several aspects of these potential changes in soil-plant-animal systems. One research direction concerns the potential for acidic precipitation to increase the incidence of selenium deficiency diseases among wild herbivores. Available literature establishes that increased sulfur input to soil-plant systems results in lower concentrations of selenium in plants and that many cultivated forages in eastern North America are already deficient in selenium by livestock dietary standards. However, several additional questions must be answered to determine if expected acidic precipitation of the future will increase the incidence of selenium deficiencies in wildlife

Interim results are presented of dose/response experiments with potted plants exposed to sulfate wash solutions with sulfate concentrations and a rate of application comparable to precipitation of eastern North America.

Other changes in browse quality due to acidification and sulfur deposition have been reported in Europe. Increased levels of metals such as mercury, cadmium and lead have been reported in areas remote from industrial pollution sources in Denmark, Sweden and Poland. A review of these findings and the potential for similar problems in Canadian wildlife are discussed.

Foliar Buffering Capacity in Boreal Species: Sources of Variability and Potential Use of Buffering Capacity for Indexing Species Sensitivity to Acidic Pollutants

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ABSTRACT

Foliar buffering capacity (B.C.) of several boreal species of various life forms (lichens to trees) was determined at nine different times from June 1980 to September 1981. B.C. varied very little diurnally and with N, S, E and W aspects. In the current year's foliage of all species, B.C. was at a maximum during the first two weeks of July and decreased gradually towards fall. In evergreen species, B.C. of previous year's foliage was half of the current year's in the spring and 20-30% lower than the current year's foliage at the end of the current growing season. The B.C. of individual trees of the same species differed significantly and the differences were consistent. In spite of the diurnal, seasonal and intra-specific variations, average B.C. differences among species were real and genetically controlled. Nutrient analysis of the foliage samples collected in spring and fall of 1980 are also presented. Relative B.C. of species is compared to reported species sensitivity to sulphur dioxide or acid rain. The potential use of B.C. for indexing species sensitivity to acid rain appears promising. However, it needs testing under simulated as well as natural conditions.

INTRODUCTION

The buffering capacity (B.C.) of species and clones has been correlated with their resistance to air pollutants and pH-changing fungi (Scholz and Knabe 1976; Scholz and Reck 1977; Scholz and Stephan 1974). Sidhu and Zakrevsky (1982) suggested that use of foliar B.C. as an index of species sensitivity to acidic air pollutants could be both convenient and economical in situations where there is a need to establish the relative sensitivity of a large number of species throughout extensive forest communities. They defined B.C. as μeq of H-ions required to change by one unit the pH of a foliage extract prepared from one gram of oven-dried foliage. They also standardized the procedure to minimize errors resulting from biological as well as field and laboratory sources during its determination. This paper deals with the sources of variations in foliar B.C. (intra- and inter-specific, diurnal, and seasonal), elemental status of foliage, and potential use of B.C. for ranking species in sensitivity to acidic air pollutants.

MATERIAL AND METHODS

Diurnal Variations in Buffering Capacity (B.C.)

Balsam fir and white birch were tested for diurnal variations in B.C. (Table 1). Five trees of each species were selected in early spring. From each tree, three branches were sampled facing north, south, east and west at 9 a.m., 12 noon and 5 p.m. In balsam fir, 1980 and 1981 growth were sampled separately. Foliage from three branches facing in each compass direction was collected, bulked together, and frozen in dry ice. However, samples from each growth year, compass direction, and tree were treated separately. The B.C. was determined by the method described by Sidhu and Zakrevsky (1982) except that titrations were performed using the 636-titroprocessor (Brinkman, Rexdale, Ontario).

Table 1. Average (± S) pH and buffering capacity of foliar extracts of balsam fir and white birch sampled at different times of the day from four aspects

Species	Growth year	Time of day	pH				Buffering capacity* (μeq H + / g foliage, O.D. weight basis)			
			N	S	E	W	N	S	E	W
Balsam fir	1981	Morning	3.75 ± 0.18	3.77 ± 0.17	3.77 ± 0.15	3.77 ± 0.16	276 ± 48	273 ± 48	281 ± 69	274 ± 60
		Noon	3.74 ± 0.11	3.77 ± 0.15	3.77 ± 0.16	3.76 ± 0.17	289 ± 48	268 ± 35	280 ± 52	267 ± 46
		Evening	3.76 ± 0.16	3.75 ± 0.14	3.75 ± 0.14	3.75 ± 0.14	279 ± 50	274 ±30	272 ± 34	267 ± 35
	1980	Morning	4.40 ± 0.19	4.33 ± 0.21	4.29 ± 0.16	4.39 ± 0.22	95 ± 18	103 ± 24	106 ± 22	99 ± 32
		Noon	4.36 ± 0.12	4.41 ± 0.26	4.40 ± 0.32	4.45 ± 0.26	100 ± 19	95 ± 28	103 ± 32	92 ± 18
		Evening	4.38 ± 0.23	4.38 ± 0.18	4.33 ± 0.19	4.42 ± 0.16	97 ± 22	98 ± 20	104 ± 24	95 ± 24
White birch	1981	Morning	4.20 ± 0.27	4.30 ± 0.34	4.25 ± 0.40	4.27 ± 0.36	276 ± 88	258 ± 102	300 ± 120	277 ± 136
		Noon	4.20 ± 0.41	4.27 ± 0.21	4.16 ± 0.23	4.18 ± 0.27	284 ± 124	280 ± 122	287 ± 103	286 ± 95
		Evening	4.23 ± 0.30	4.32 ± 0.25	4.17 ± 0.21	4.17 ± 0.28	284 ± 98	294 ± 144	276 ± 73	291 ± 113

* Buffering capacity is μeq H-ions required to change the pH of foliage extract equivalent to one gram of oven-dried foliage by one pH unit (Sidhu and Zakrevsky 1982).

Seasonal and Inter-specific Variations

Buffering capacity determined in 1979 for 18 forest species indicated large inter- specific differences and warranted the study of annual and seasonal variations within species. In the last week of May 1980, five individuals or clumps (shrubs and lichens) of each species (Table 2) were tagged for long-term sampling. Species were located within a circle of 50-metre radius in an open balsam fir and black spruce forest stand. The foliage from five individuals of each species was sampled twice during 1980 and seven times during 1981. Samples from each individual, each growth year, and each sampling time were treated separately. Species and sampling dates are listed in Table 2.

B.C. and Foliar Nutrient Analysis

Foliar samples of nine species collected in June and August of 1980 for B.C. determinations were also analyzed for foliar nutrient concentrations.

The subsamples for nutrient analysis were dried at 70°C for at least 48 hours and ground to pass through 40 mesh screen. The ground samples were analyzed for F, Ca, Mg, K, Na, Al, Fe, Zn, Cd, Mn, Cu, Ni, P, S, and N.

For cation determination, a 1.0 g sample was ashed at 475°C, the residue digested in HF, then evaporated to dryness and redissolved in 1 ml of aqua regia (1 ml HNO_3:3 ml HCl). This was diluted to 100 ml and analyzed spectrophotometrically.

Total N and P were determined colorimetrically. Each sample was digested in a mixture of concentrated H_2SO_4 (25 ml) containing a catalyst (10 g in the proportion of 15 g K_2SO_4:0.7 g HgO) at 390°C on a block digester for 2 hours. The digest was diluted to 250 ml with H_2O and analyzed for N and P simultaneously by an automated colorimetric method (Technicon Insustrial Systems. 1976).

Total sulphur was determined by ion chromatography. A 0.10 g sample was combusted in a Schöniger flask and the resulting gas absorbed in 25 ml H_2O containing 4-5 drops of H_2O_2. The resulting solution was analyzed for sulphur by ion chromatography (Zakrevsky and Sidhu 1982).

For total fluorides, 1.0 g of foliar sample was ashed in the presence of 0.02 g of CaO at 450°C, then fused with NaOH and dissolved in HCl. The pH was adjusted to 5.7 and volume to 50 ml. Fluoride in the solution was measured using a F-ion specific electrode (Buck and Reusman 1971; Sidhu 1979).

RESULTS AND DISCUSSION

Diurnal Variations

The average pH and B.C. of foliar extracts of balsam fir and white birch for different times of the day and compass directions are given in Table 1. For balsam fir, the pH of the current year's foliage was, on average, 0.6 pH units lower than that of the previous year's foliage. The differences in pH among individuals varied from 0.11 to 0.18 units in the current year's foliage and 0.12 to 0.32 units in the previous year's foliage. The B.C. in the current year's foliage, however, was 2.7 to 3.0 times that of the previous year's foliage. The pH and B.C. varied little with time of day and the exposure (Table 1).

The B.C. differences among individual white birch trees were much greater than in balsam fir (Table 1). The pH of foliar extracts was higher in white birch than in balsam fir. On a diurnal basis, B.C. varied by 9-14% of the lowest value during the day. In the morning, foliar samples from branches

Table 2. Mean (± S) pH and buffering capacity (B.C.) of foliage from tagged individuals of selected boreal species from June 1980 to October 1981

		Date sampled								
Species, growth year	Para-meter	16 June 1980	20 Aug. 1980	9 June 1981	23 June 1981	7 July 1981	21 July 1981	4 Aug. 1981	19 Aug. 1981	1 Sep. 1981
Balsam fir,⁺	pH	4.15 ± 0.20	3.96 ± 0.23	4.93 ± 0.29	4.72 ± 0.27	4.55 ± 0.29	4.44 ± 0.18	4.44 ± 0.19	4.39 ± 0.20	4.44 ± 0.12
1980	B.C.	204 ± 35	132 ± 39	62 ± 22	69 ± 22	82 ± 22	88 ± 18	100 ± 24	109 ± 26	102 ± 26
Balsam fir,⁺	pH	-	-	4.01 ± 0.16	3.75 ± 0.13	3.64 ± 0.16	3.95 ± 0.17	3.98 ± 0.14	4.10 ± 0.23	4.15 ± 0.22
1981	B.C.	-	-	207 ± 34	241 ± 49	245 ± 41	143 ± 45	144 ± 38	124 ± 35	122 ± 39
Black spruce,⁺	pH	3.85 ± 0.13	3.97 ± 0.27	4.88 ± 0.16	4.81 ± 0.40	4.53 ± 0.10	4.47 ± 0.13	4.34 ± 0.08	4.38 ± 0.20	4.44 ± 0.09
1980	B.C.	244 ± 62	158 ± 34	69 ± 14	65 ± 14	99 ± 13	113 ± 14	108 ± 15	117 ± 16	117 ± 29
Black spruce,⁺	pH	-	-	3.98 ± 0.18	3.41 ± 0.10	3.45 ± 0.10	3.88 ± 0.19	3.89 ± 0.33	4.01 ± 0.25	4.20 ± 0.32
1981	B.C.	-	-	278 ± 44	479 ± 58	391 ± 87	216 ± 57	185 ± 48	161 ± 41	145 ± 29
Larch, 1980⁺	pH	3.72 ± 0.09	3.80 ± 0.10	-	-	-	-	-	-	-
	B.C.	411 ± 27	338 ± 29	-	-	-	-	-	-	-
Larch, 1981⁺	pH	-	-	3.45 ± 0.04	3.48 ± 0.06	3.48 ± 0.07	3.71 ± 0.08	3.76 ± 0.09	3.81 ± 0.12	4.09 ± 0.14
	B.C.	-	-	366 ± 27	332 ± 38	327 ± 40	261 ± 23	245 ± 29	231 ± 28	204 ± 39
White birch,⁺	pH	5.00 ± 0.27	5.10 ± 0.33	-	-	-	-	-	-	-
1980	B.C.	119 ± 54	118 ± 63	-	-	-	-	-	-	-
White birch,⁺	pH	-	-	4.99 ± 0.38	4.61 ± 0.31	4.61 ± 0.37	4.95 ± 0.27	5.50 ± 0.29	5.25 ± 0.24	5.39 ± 0.10
1981	B.C.	-	-	132 ± 105	182 ± 121	150 ± 90	134 ± 61	116 ± 64	96 ± 43	79 ± 27
Alder, 1980*	pH	5.68	5.65	-	-	-	-	-	-	-
	B.C.	93	96	-	-	-	-	-	-	-
Alder, 1981*	pH	-	-	5.49	4.84	5.06	5.02	5.12	5.05	5.43
	B.C.	-	-	101	125	115	118	85	93	88
Kalmia, 1980*	pH	5.14	4.69	-	-	-	-	-	-	-
	B.C.	65	74	-	-	-	-	-	-	-
Kalmia, 1981*	pH	-	-	5.72	5.46	4.74	4.63	4.67	4.59	4.74
	B.C.	-	-	64	52	82	97	92	78	77
Blueberry,*	pH	3.31	3.38	-	-	-	-	-	-	-
1980	B.C.	577	585	-	-	-	-	-	-	-
Blueberry,*	pH	-	-	3.25	3.28	3.26	3.36	3.31	3.52	3.72
1981	B.C.	-	-	616	611	586	511	500	422	471
Raspberry,*	pH	5.61	5.73	-	-	-	-	-	-	-
1980	B.C.	91	90	-	-	-	-	-	-	-
Raspberry,*	pH	-	-	5.24	5.23	5.21	5.32	5.47	5.60	5.53
1981	B.C.	-	-	134	124	96	72	77	75	64
*Cladonia**	pH	4.54	4.34	-	-	-	-	-	-	-
alpestris, 1980	B.C.	15	21	-	-	-	-	-	-	-
*C. alpestris**,	pH	-	-	4.69	4.27	4.50	4.29	4.10	4.15	4.21
1981	B.C.	-	-	11	20	30	22	21	24	20

+ Standard deviation is measure of differences among individuals of the same species. Foliage samples from each individual analyzed separately.
* Bulk sample from five individuals per species analyzed for pH and B.C.

facing east exhibited the highest B.C., whereas the lowest B.C. occurred in samples from south-facing branches. In the evening, B.C. was at a maximum in foliage from south-facing branches and least in foliage from the east-facing branches. The difference due to compass directions was least in samples collected at noon time. Based on these observations, it is recommended that sampling of foliage for B.C. determinations is done at noon time.

Seasonal and Annual Variations

From a preliminary study in 1979, the nine species listed in Table 2 were sampled over a two-year period to determine the degree of intra- and inter-specific, seasonal, and annual variation in B.C. and the pH of their foliar extracts. The results are summarized in Table 2 for the 16 June 1980 to 1 September 1981 period.

Variations in pH and B.C. of the current year's foliage of conifer, deciduous, and ericaceous species followed similar patterns. For example, the average B.C. in the current year's balsam fir foliage was at a maximum 4-5 weeks after bud break and decreased by 50% towards fall. The pH varied inversely with the B.C. Buffering capacity in the previous year's foliage was at a minimum in spring and gradually reached its maximum in the first half of August (Table 2). Individuals differed from one an other but followed similar patterns during the growing season (Fig. 1). The pattern of variation in black spruce was similar to that in balsam fir (Table 2, Fig. 2). However, B.C. was higher and pH was lower than in balsam fir. Spring to fall variations in B.C. of larch, as well as of broad-leaved species, followed the general pattern in balsam fir (Fig 3). Variations from spring to fall were not as great as in balsam fir and the maxima and minima in different species appeared a little later or earlier during the growing season. Despite all these intra-specific, seasonal, and annual variations, differences among species were significant and consistent under natural conditions. As a result, B.C. offers potential as an indicator of species' relative sensitivity to acidic pollutants.

There was no linear relationship between pH and B.C. of foliar extracts. However, certain characteristics were exhibited by single species and species groups (Table 2):

(i) In all conifers, current year's growth had the highest B.C. in spring and early summer and the least in the fall. Older growth, however, had the lowest B.C. in spring. The B.C. gradually increased towards fall and remained 20-30% lower than that of the current year's growth. In most cases, pH was higher when B.C. was lower and vice versa.

(ii) pH of foliar extracts of broad-leaved deciduous species was usually higher than that of evergreens except in blueberry. This species showed the highest B.C. and lowest pH among all the species included in the study. In general, B.C. in these species was lower than in conifers and decreased from spring to fall.

(iii) In *Cladonia* and other lichens, the B.C. was very low and pH of the extracts was intermediate between the evergreen conifers and broad-leaved deciduous species.

B.C. and Foliar Nutrient Status

The results of the nutrient analysis of B.C. samples for 1980 are presented in Table 3. The B.C. did not correlate significantly ($P = 0.10$) with any of the elements listed in Table 3. The variations in elemental concentrations were either seasonal or specific in nature.

Fluoride in all cases was less than 10 ppm and remained at the normal concentrations in all species in spring as well as fall. Calcium and magnesium exhibited a typical pattern of gradual increase from spring to fall in the current year's growth of conifers and broad-leaved species. These results are similar to those reported by others (Kramer and Kozlowski 1960; Likens and Bormann

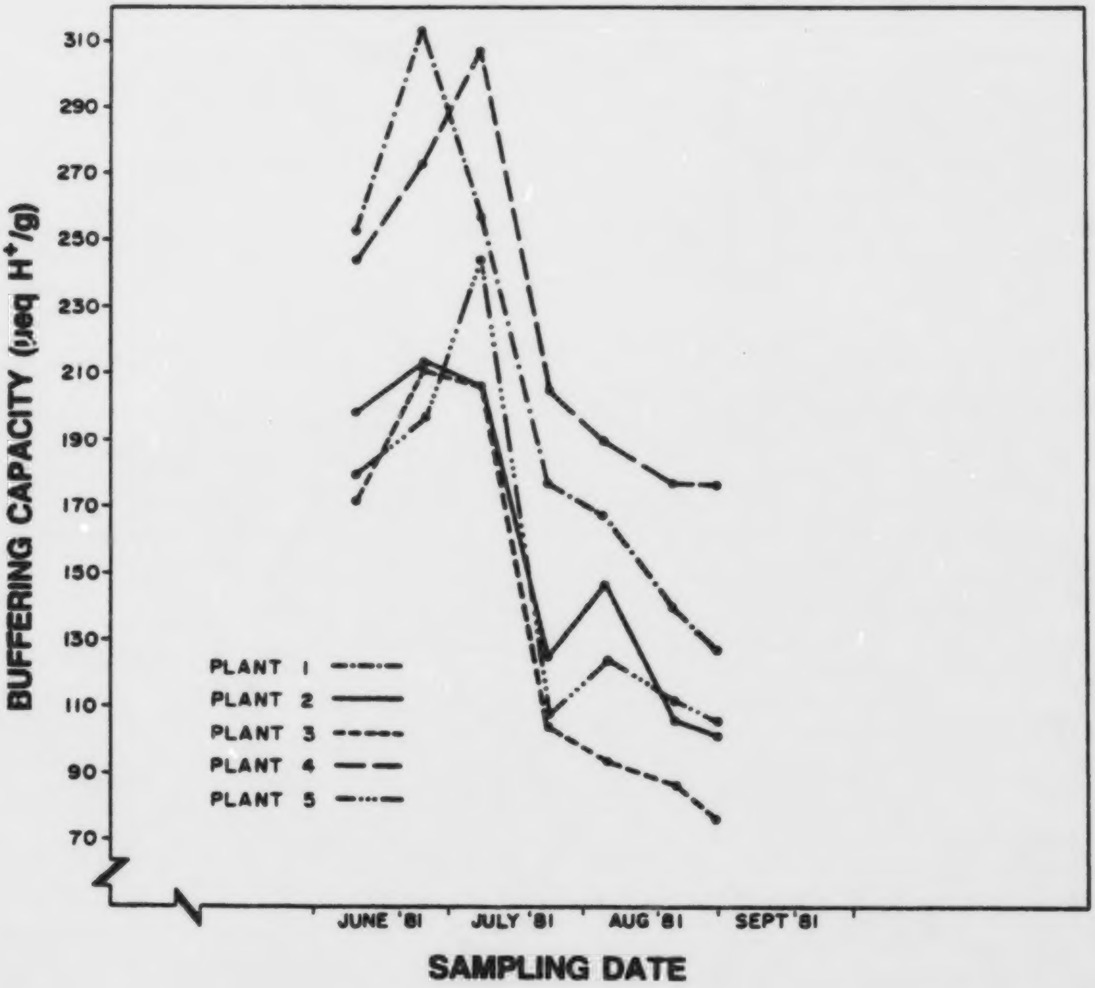

Figure 1. Average buffering capacity of foliar extracts of five different individuals of balsam fir, 1981 growth

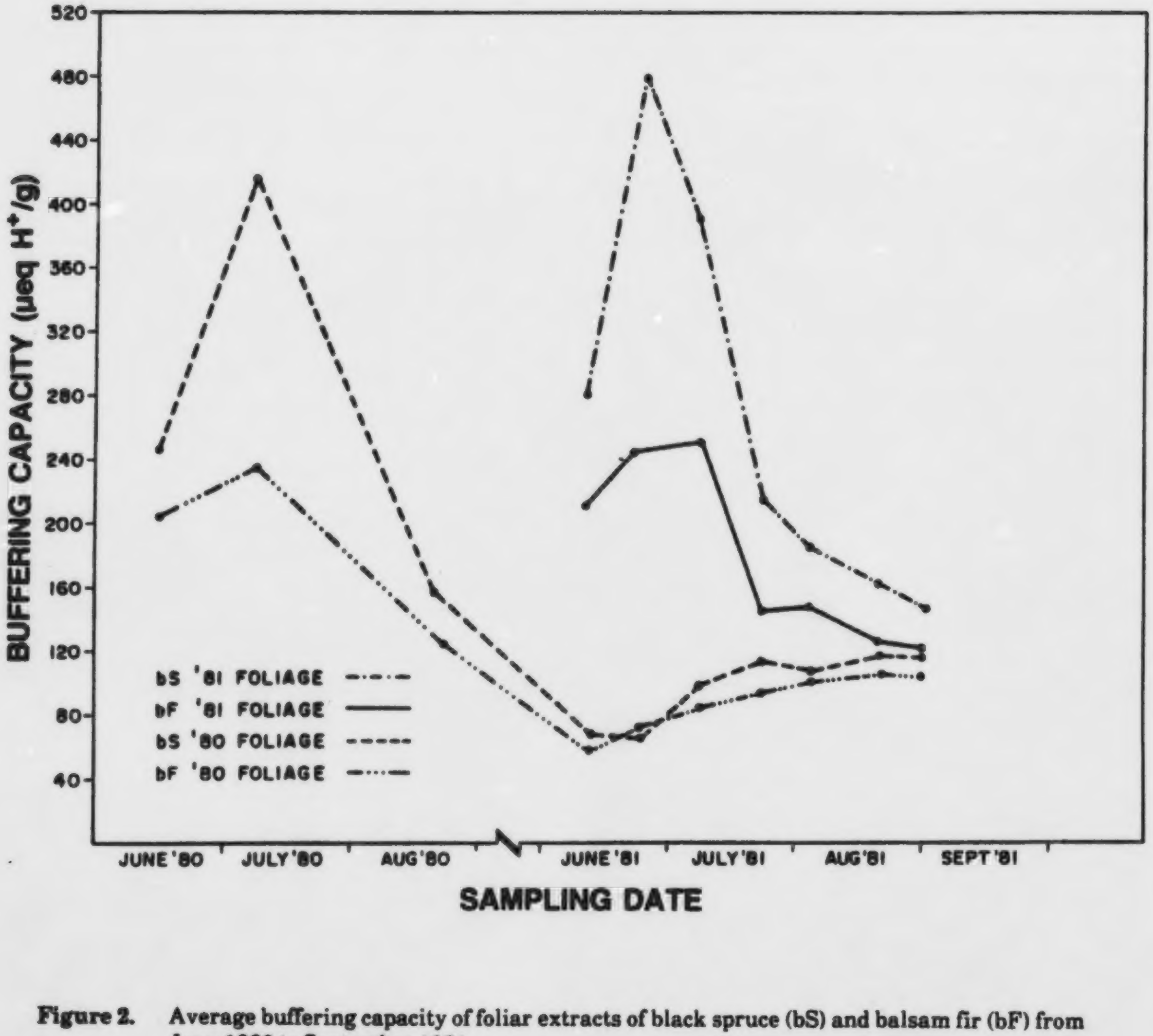

Figure 2. Average buffering capacity of foliar extracts of black spruce (bS) and balsam fir (bF) from June 1980 to September 1981

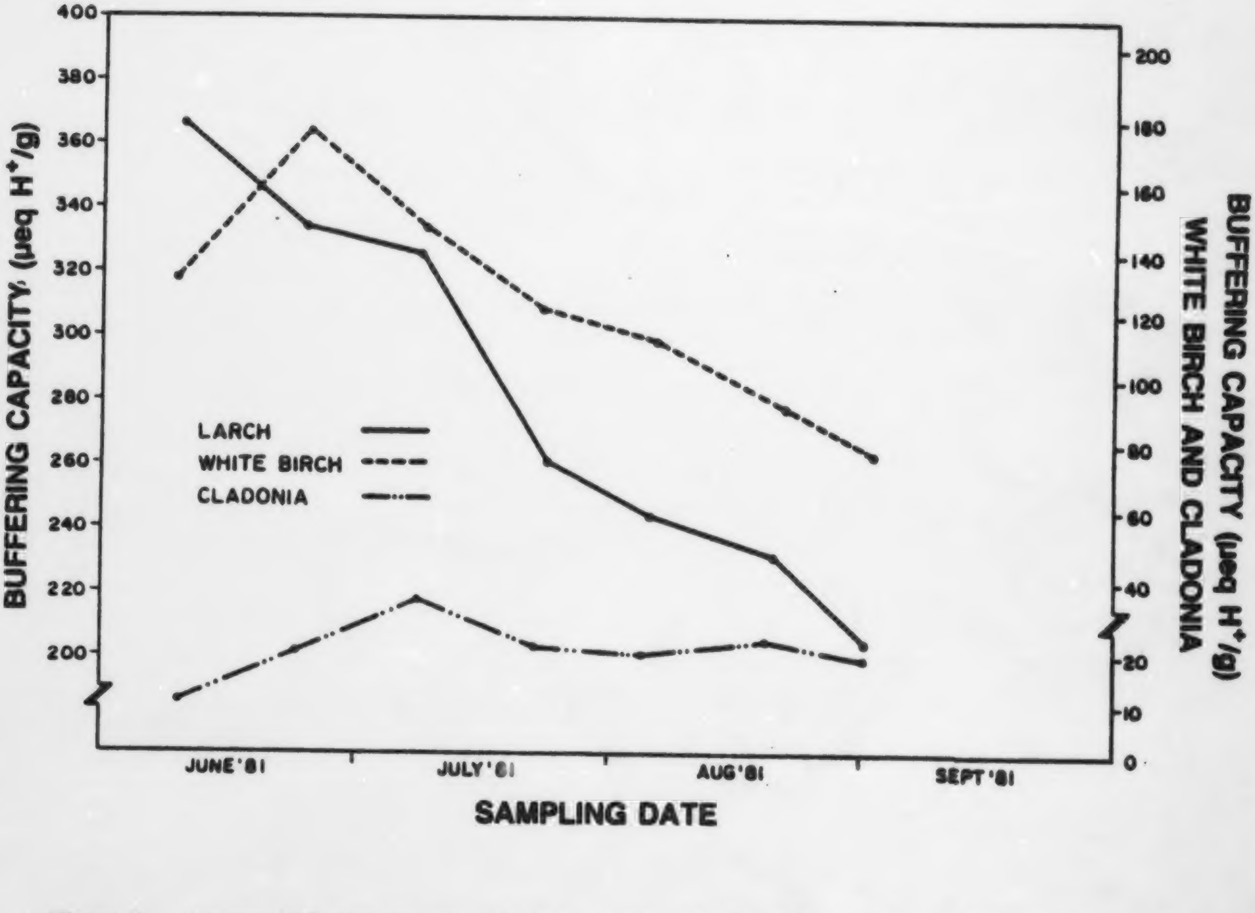

Figure 3. Average buffering capacity of foliar extracts of larch, white birch, and Cladonia 1981 growth

Table 3. Buffering capacity (B.C.) and average [+] concentration of selected elements in foliage of boreal plants sampled in spring and fall of 1980, Norman's Cove, Newfoundland

Species	Growth year	Sampling date	pH foliar extracts	B.C. foliar extracts	Concentration (± S) of elements (ppm, o.d.w. basis)												%
					F	Ca	Mg	K	Na	Al	Fe	Zn	Mn	Cu	P	S	N
Balsam fir	1979	16 Jun '80	4.97 ± 0.29	55 ± 20	6.0 ± 2.5	5654 ± 1142	609 ± 40	3737 ± 476	295 ± 123	321 ± 85	68 ± 25	33 ± 7	1180 ± 198	9 ± 4.0	454 ± 130	734 ± 81	0.77 ± 0.09
		20 Aug '80	4.45 ± 0.19	102 ± 27	4.8 ± 0.6	5929 ± 1480	860 ± 157	4092 ± 515	380 ± 134	424 ± 194	130 ± 52	43 ± 9	1363 ± 319	5 ± 1.0	1120 ± 190		1.04 ± 0.18
	1980	16 Jun '80	4.15 ± 0.20	204 ± 35	5.7 ± 2.7	855 ± 75	804 ± 164	12896 ± 759	169 ± 67	244 ± 40	50 ± 21	43 ± 6	172 ± 21	8 ± 2.0	3854 ± 390	1596 ± 129	2.06 ± 0.32
		20 Aug '80	3.96 ± 0.23	132 ± 39	4.1 ± 0.8	3569 ± 726	755 ± 115	4710 ± 332	456 ± 128	309 ± 119	111 ± 94	33 ± 4	714 ± 222	6 ± 2.0	1150 ± 150	-	1.01 ± 0.18
Black spruce	1979	16 Jun '80	4.59 ± 0.13	58 ± 6	7.0 ± 0.6	4657 ± 1011	580 ± 56	3399 ± 593	399 ± 113	135 ± 12	53 ± 8	48 ± 13	1667 ± 421	6 ± 2.0	408 ± 130	622 ± 42	0.73 ± 0.04
		20 Aug '80	4.60 ± 0.07	101 ± 11	5.0 ± 1.2	6084 ± 2131	798 ± 348	2529 ± 712	598 ± 188	119 ± 40	118 ± 28	44 ± 23	979 ± 715	5 ± 0.1	900 ± 140	-	0.98 ± 0.04
	1980	16 Jun '80	3.85 ± 0.13	244 ± 62	6.0 ± 2.5	1361 ± 206	672 ± 67	6869 ± 735	307 ± 41	50 ± 15	43 ± 15	29 ± 3	447 ± 87	7 ± 2.0	1935 ± 40	868 ± 49	1.09 ± 0.10
		20 Aug '80	3.97 ± 0.27	158 ± 34	3.9 ± 0.8	2112 ± 363	748 ± 145	5202 ± 447	271 ± 109	100 ± 33	94 ± 78	34 ± 4	1592 ± 718	5 ± 0.7	1240 ± 130	-	0.82 ± 0.40
Larch	1980	16 Jun '80	3.72 ± 0.09	411 ± 27	7.8 ± 1.0	1415 ± 250	544 ± 103	17089 ± 1103	478 ± 62	135 ± 22	95 ± 31	42 ± 2	555 ± 265	11 ± 3.0	5185 ± 470	2228 ± 83	3.15 ± 0.25
		20 Aug '80	3.80 ± 0.11	338 ± 29	5.9 ± 0.3	2439 ± 585	1322 ± 210	4549 ± 583	967 ± 555	333 ± 89	188 ± 47	25 ± 7	553 ± 388	8 ± 0.2	1820 ± 340	-	1.54 ± 0.08
White birch	1980	16 Jun '80	5.24 ± 0.28	119 ± 55	9.2 ± 2.2	2780 ± 1521	2058 ± 359	11950 ± 1199	454 ± 138	-	89 ± 14	-	1463 ± 590	14 ± 2.0	5412 ± 737	2788 ± 303	3.79 ± 0.30
		20 Aug '80	5.12 ± 0.30	118 ± 63	5.2 ± 0.9	5597 ± 2643	2707 ± 614	6374 ± 1509	536 ± 96	109 ± 25	134 ± 31	20 ± 7	2557 ± 667	9 ± 0.2	2470 ± 450	-	2.32 ± 0.18
Alder	1980	16 Jun '80	5.68	93	8.9	2989	2380	11625	444	115	134	64	498	18.0	4869	2697	3.71
		20 Aug '80	5.65	96	5.7	4532	3628	5665	517	116	193	59	1161	9.0	2020	-	3.08
Blueberry	1980	16 Jun '80	3.31	577	8.8	2753	1147	9558	229	191	151	42	2141	12.0	3819	2243	2.96
		20 Aug '80	3.38	586	5.8	6012	2464	3252	453	199	422	28	2759	9.0	1280	-	1.64
Kalmia	1980	16 Jun '80	5.14	65	7.2	2980	1192	2981	258	174	85	15	1575	6.0	932	823	1.11
		20 Aug '80	4.69	104	4.3	6918	1037	4249	207	754	65	14	-	8.0	1280	-	1.36
Raspberry	1980	16 Jun '80	5.61	91	8.3	6143	2510	17891	752	895	68	68	1691	13.0	4438	2257	3.95
		20 Aug '80	5.73	90	6.0	5477	5245	10102	388	472	259	49	1360	9.0	2680	-	2.26
Cladonia	1979/80	16 Jun '80	4.54	15	7.5	675	299	1796	167	399	285	12	23	2.0	394	448	0.47
		20 Aug '80	4.34	21	5.3	279	149	1295	80	377	341	8	20	4.0	590	-	0.38

[*] Concentrations of Cd and Ni in all samples were < 0.1 ppm
[+] Average of 5 individuals for each species

1970; Gosz et al. 1972). Raspberry and *Cladonia* were the exceptions. Concentrations of potassium, phosphorus, and nitrogen decreased from spring to fall except N and P in the current year's growth of conifers, *Kalmia*, and lichens. In the latter case there was an increase or insignificant decline from spring to fall. Among the other cations analyzed, aluminum and iron increased from spring to fall and copper decreased in fall, in most cases. Manganese showed no consistent pattern. There was no change in cadmium and nickel.

Sulphur values were only available for spring samples at the time of writing.

B.C. and Relative Sensitivity of Plant Species to Acidic Pollutants

The 18 species studied during 1979 differed significantly in B.C. At the time, no published reports were available on these species' relative sensitivity to acid rain. The 18 were ranked according to their relative B.C. and calculated relative sensitivity indices (1 x 100/rel. B.C.). The lichens, known to be highly sensitive to SO_2, had the lowest B.C. and highest sensitivity index. The broad-leaved species, like alder (*Alnus crispa*) and white birch (*Betula papyrifera*), had intermediate B.C. Conifers exhibited high B.C. These characteristics parallel the fact that broad-leaved species are more sensitive than the conifers to SO_2 and other acidic pollutants. The relative ranking of 18 species is presented in Table 4.

The ranking of selected species based on their relative B.C. compared favorably with their ranking in order of sensitivity to SO_2, reported by Malhotra and Addison (1979) and presented below:

Sensitivity ranking based on SO_2 symptom development under fumigation	Sensitivity rating based on relative B.C.
Paper birch	Green alder
Green alder	Paper birch
Jack pine	-
Labrador tea	Labrador tea
White and black spruce	Black spruce

The relative B.C. can only be used as an index of sensitivity if sensitivity ratings based on B.C. remain fairly consistent from site to site and year to year. The relative sensitivities of nine species based on B.C. measurements at four different times are presented in Table 5. Although the absolute values of relative sensitivity varied, their ranking on the sensitivity scale did not change. Based on the information available at present, B.C. shows good potential as an index of relative sensitivity of species to acid rain. However, tests would have to be conducted under simulated and natural conditions.

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Table 4. Buffering capacity, relative buffering capacity, and sensitivity of selected boreal forest species from Newfoundland

Species	16 July 1979		
	B.C.*	Rel. B.C.**	S.I.***
Ramalina minuscula (Nyl.) Nyl.	11	0.51	196
Cladonia rangiferina (L.) Wigg.	14	0.65	154
C. mitis Sandst.	16	0.74	135
C. alpestris (L.) Rabenh.	16	0.74	135
Cetraria ciliaris Ach.	26	1.20	83
Usnea longissima (L.) Ach.	29	1.34	75
Hypogymnia physodes (L.) Nyl.	34	1.57	64
Alectoria nidulifera Norrl.	50	2.31	43
Kalmia angustifolia L.	90	4.17	24
Rubus idaeus L.	94	4.35	23
Alnus crispa (Ait.) Pursh	109	5.05	20
Betula papyrifera Marsh.	144	6.67	15
Sorbus americana Marsh.	156	7.27	14
Ledum groenlandicum Oeder	196	9.07	11
Abies balsamea (L.) Mill.	226	10.46	10
Picea mariana (Mill.) B.S.P.	240	11.11	9
Larix laricina (Du Roi) K. Koch	268	12.41	8
Vaccinium angustifolium Ait.	441	20.42	5

* B.C. = Buffering capacity

** Rel. B.C. = $\frac{\text{B.C. of species (i)}}{\Sigma_i \text{B.C.}} \times 100$

*** S.I. = Sensitivity index = $\frac{1}{\text{Rel. B.C.}} \times 100$

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Table 5. Buffering capacity and sensitivity indices of selected boreal forest species from Newfoundland

Species	16 July 1979		20 June 1980		20 August 1980		1981 average (14 wk)*	
	B.C.**	S.I.***	B.C.	S.I.	B.C.	S.I.	B.C.	S.I.
Cladonia alpestris (L.) Rabenh.	16	102.0	15	120.5	21	71.4	21	80.0
Kalmia angustifolia L.	90	18.1	65	27.9	74	20.2	77	23.9
Rubus idaeus L.	94	17.3	91	20.0	90	16.6	92	18.2
Alnus crispa (Ait.) Pursh	109	14.9	93	19.5	96	15.6	103	16.2
Betula papyrifera Marsh.	144	11.3	119	15.3	118	12.7	127	13.1
Abies balsamea (L.) Mill.	226	7.2	204	8.9	132	11.4	175	9.6
Picea mariana (Mill.) B.S.P.	240	6.8	242	7.5	146	10.3	265	6.3
Larix laricina (Du Roi) K. Koch	268	6.1	411	4.4	238	6.3	280	6.0
Vaccinium angustifolium Ait.	441	3.7	577	3.1	585	2.6	531	3.1

* 1981 - average B.C. = mean of seven samples collected between 9 June and 1 September 1981

** B.C. = buffering capacity

*** S.I. = $(\Sigma_i \text{B.C.})/\text{B.C. Sp}_i$

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Does Ozone Disturb Water Balance in Forest Trees in Sweden?

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INTRODUCTION

Since 1976 spruce needles in southern Sweden have exhibited symptoms similar to those caused by drought (Barklund 1983). In 1982 pine needles in southern forests fell off earlier than expected, and in 1983 many spruce forests in southern Sweden exhibited the same symptoms.

A few different hypotheses have been suggested as explanations for these symptoms. The most realistic hypothesis is the one that suggests drought as the cause, because the summers of 1976 and 1982 were very dry and hot.

However, drought does not seem to be the only explanation for the extensive damage in 1982 and 1983. One possibility that has not yet been tested is that ozone might play an important role in the observed drought damage.

Ozone monitoring on the Swedish west coast, which started in 1972, shows that ozone episodes (120-400 $\mu g\ m^{-3}$) occur frequently every summer.

Many air pollution research workers have measured the short-term effects of high levels of ozone ($> 250\ \mu g\ m^{-3}$) on trees. However, few have examined effects of lower levels during a longer time (National Research Council 1977). High levels of ozone very often cause visible symptoms, although lower levels during a growing season might cause invisible changes, such as excess water loss and decreased growth.

Our research work started in March 1983 with the pilot study presented here. The hypothesis of the study is that ozone affects the stomatal mechanism in conifers in such a way that the transpiration rate is disturbed. As a result, the tree's ability to maintain its water balance is disturbed, especially during a drought period, when ozone is present.

MATERIALS AND METHODS

Scots pine (*Pinus sylvestris* L.) seedlings were exposed for six weeks to simulated ozone levels and episodes (80-240 $\mu g\ m^{-3}$) typical of those occurring on the Swedish west coast every summer. Afterwards, seedlings were subjected to drought (water stress).

The exposure system consisted of four, 3-litre, water-cooled, "Perspex" glass chambers. Seedlings were enclosed in the chambers and grown at 24°C (17-hour day) and 19°C (7-hour night) and in a relative humidity of 45-50%.

The air (30 L min^{-1}) was cleaned with four different filters (charcoal, Purafil, K_2CO_3, and oxalic acid) to remove particles, SO_2, NO_x, NH_3, O_3, and organic substances. Concentration of ozone was measured before and after the air was introduced into three of the chambers. The fourth chamber was used as a control with clean air only. Photosynthesis and transpiration were measured periodically.

RESULTS

Photosynthesis rate was not affected. The ozone levels and transpiration rates of both control and exposed seedlings during the entire experimental period are presented in Figure 1.

After 4 weeks of exposure to 80 μg m^{-3}, including four episodes with a maximum concentration of 240 μg m^{-3}, the rate of transpiration increased during the light period (Figures 1 and 2). A week later, transpiration also occurred during the dark period in the ozone-exposed seedlings. The seedlings were exposed to one more ozone episode and afterwards put under water stress and ozone stress. The ozone-exposed seedlings continued to transpire 10 % more than the control. After 2 days of water stress, transpiration and photosynthesis stopped in the ozone-exposed seedlings. The control seedling was still alive when the experiment finished (Figure 1).

DISCUSSION

Accumulated water loss during the 6-week period was 110 g g^{-1} (dw) in the exposed seedlings and 100 g g^{-1} (dw) in the control.

If this difference is significant, ozone might have an important influence on the ability of pine trees to keep their water balance in areas with frequently high ozone levels ($\leq$ 240 μg m^{-3}). Ozone levels used in this pilot study were not extremely high. Ozone episodes can occur with concentrations of about 300-400 μg m^{-3} for several days. Moreover, such levels of ozone can occur several times during a season (May-September).

These results are preliminary and the experiment will be repeated. The same hypothesis will also be tested on spruce (*Picea abies*) seedlings.

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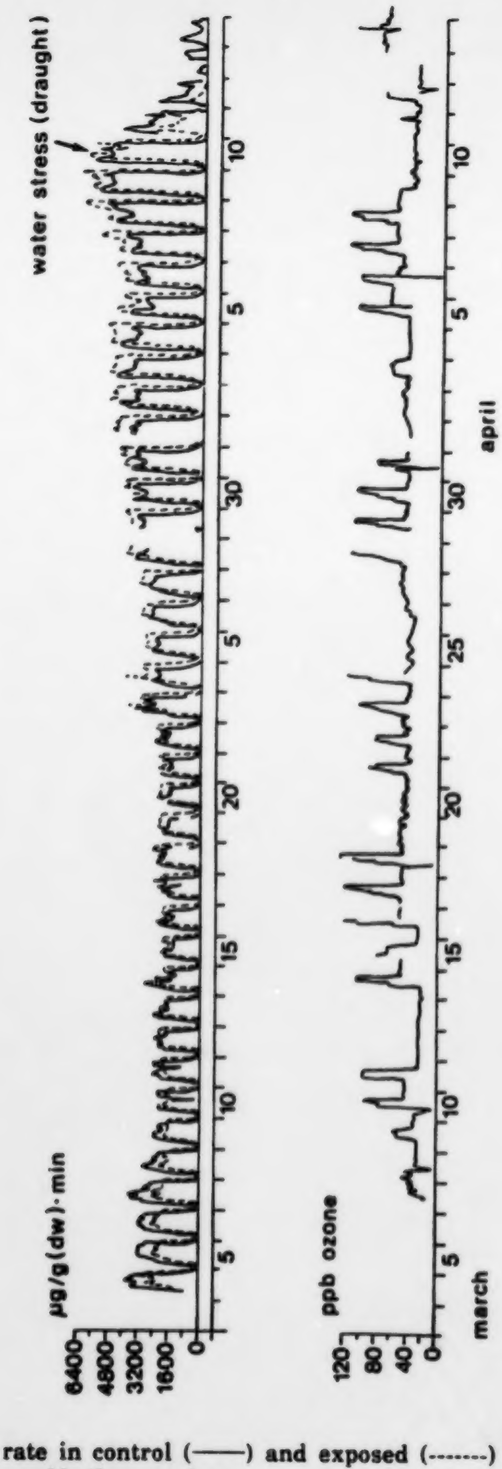

Figure 1. Transpiration rate in control (——) and exposed (-------) pine seedlings and ozone concentrations used in the experiment.

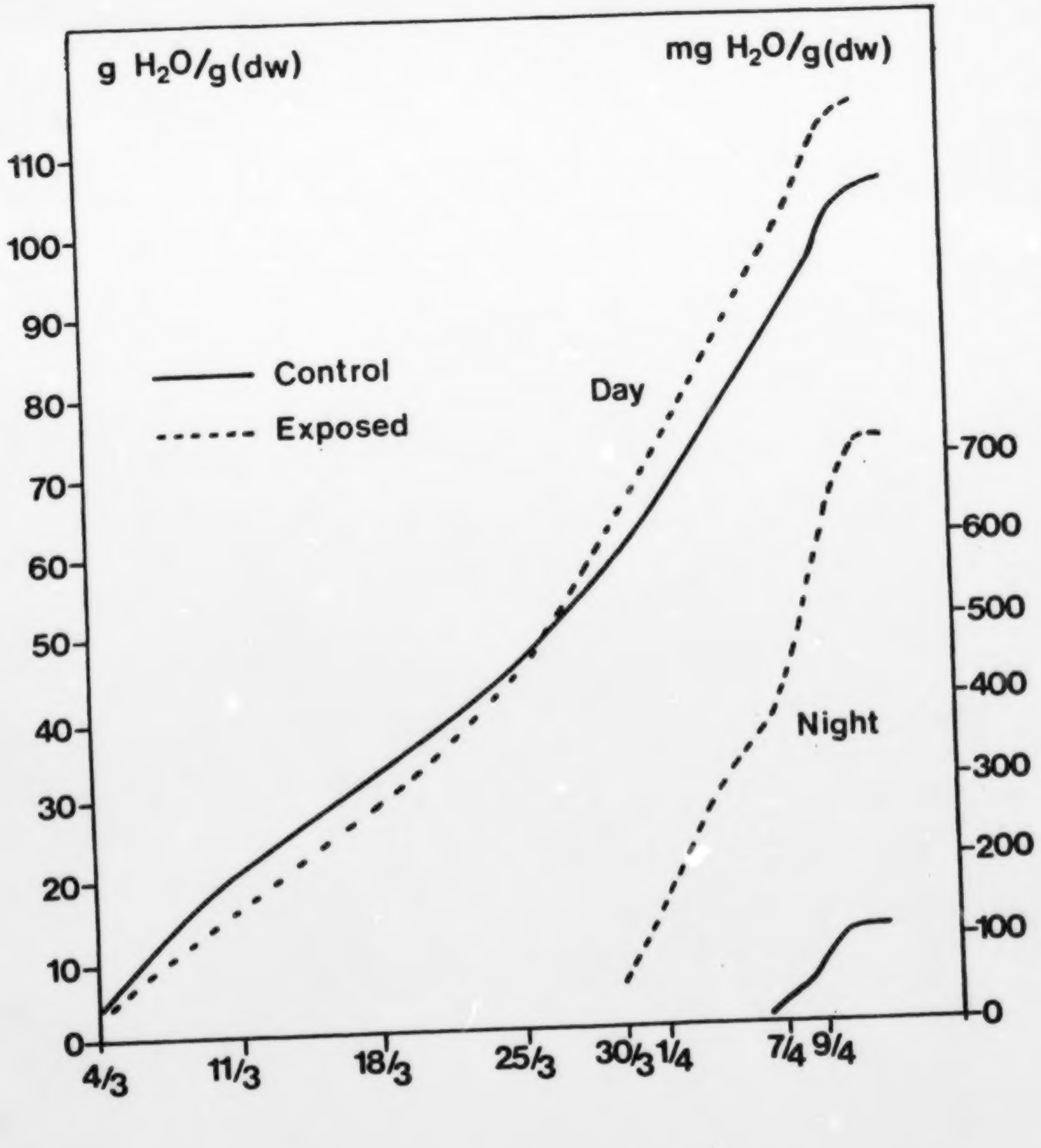

Figure 2. Accumulated water loss in pine seedlings during the experiment.

Effects of Ozone on Scots Pine (*Pinus sylvestris*) and Spruce (*Picea abies*)

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ABSTRACT

Deposition and effects of ozone on seedlings of Scots pine and spruce were investigated. The pine seedlings were exposed during 6 weeks to simulated ozone levels and episodes (80-240 µg m^{-3}) that occur on the Swedish west coast every summer. The spruce seedlings were exposed to ozone during 2 weeks to two simulated ozone episodes with maximum levels of 240 µg m^{-3}. After exposure the plants were kept in exposure chambers and put under water stress to study their ability to survive. Uptake, net photosynthesis, respiration and transpiration rates were measured. The uptake of ozone increased with increased ozone concentration, being directly proportional to it. Ozone affects the stomatal mechanism of the seedlings, resulting in increased transpiration after an ozone episode. Water stress on the plants resulted in an earlier death (2-4 days) in the ozone-exposed plants compared to the control.

Heavy Metal Contamination of Terrestrial Ecosystems from Long-range Atmospheric Transport

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ABSTRACT

The deposition of some toxic elements has been shown to be substantially higher in the southernmost part of Norway than in areas farther north, mainly because of transport of polluted air from other parts of Europe. Natural surface soils have been shown to exhibit a very similar geographical pattern with respect to the same group of elements. For example, the surface soil Pb content is about 10 times higher in the far south than in parts of central and northern Norway, not appreciably affected by long-range atmospheric transport of pollutants. Studies of the vertical distribution of metals in soil profiles from different parts of the country lend further support to the idea of atmospheric deposition being the main source of excess Pb and Cd in surface soils of southern Norway. A comparison of coniferous forest ecosystems in southern and central Norway with respect to heavy metal contents of common species of higher plants shows a similar trend as for soils. Concerning Pb and Cd, plants from localities in southernmost Norway show substantially higher contents than those from equivalent localities in central Norway, the difference in many cases amounting to a factor of 5 or more. The essential elements Cu and Zn do not exhibit a similar trend.

INTRODUCTION

Investigations carried out during the past decade have convincingly demonstrated that the southernmost part of the Scandinavian peninsula is considerably affected by "acid precipitation" transported from highly industrial areas mainly in central and western Europe. The wet deposition of "excess sulfate" in southernmost Norway in 1980 was, for example, about 10 times higher than in the northern part of the country (Overrein et al. 1980). The main reason for this large difference is that the precipitation in southern Norway occurs predominantly with wind from the southeast through southwest. On the other hand, westerly and northwesterly winds carrying relatively clean air from the Norwegian Sea are mainly responsible for the precipitation in central and northern Norway.

The heavy metal air pollution in Norway has been extensively studied on a national basis, by means of air particulate samples (air concentrations), precipitation (wet deposition), and moss samples (relative deposition figures). Through these and other studies (Hanssen et al. 1980; 1981, Rambaek and Steinnes 1980), the following important trends have become evident:

a. The deposition of many elements is significantly higher in the southern and southwestern parts of the country than in areas farther north. For some relatively volatile elements (Pb, Cd, As), this difference amounts to a factor of about 10.

b. A large part of this trace element deposition is due to long-range atmospheric transport from other parts of Europe, as is the case with "excess sulfate". For the above group of elements, long-range transport is the predominant source of atmospheric deposition in Norway.

HEAVY METALS IN NORWEGIAN SURFACE SOILS

In 1977, samples of natural surface soils were collected from about 500 sites distributed evenly over the country. More than 70% of the samples were from podzol profiles, showing high organic-matter contents (50-90%). This material has been analyzed with respect to about 25 elements (HNO_3-soluble fraction). Some of these elements show a similar and rather characteristic geographic distribution in the surface soil, as illustrated in the case of Pb in Fig. 1. The distribution trend appears to be very similar to that of the atmospheric deposition of Pb, indicating that the Pb content of surface soils in southern Norway is, to a great extent, dependent on long-range atmospheric supply (Allen and Steinnes 1980). Corresponding trends are evident for As, Sb, and Cd, but the less volatile elements, Cu and Zn, do not show similar large regional differences.

Strong support for the theory of atmospheric supply as the main source of these volatile trace elements to natural surface soils in southern Norway comes from a study of peat profiles from 21 ombrotrophic bogs in different parts of Norway (Hvatum et al. 1983). Whereas the surface peat in general shows concentrations similar to soils in the same area for the elements studied, levels of the volatile elements are substantially lower at a 20- to 50-cm depth, the vertical gradient being most pronounced for bogs in southern Norway.

FURTHER STUDY OF SURFACE SOILS

As evident from Fig. 1 in the case of Pb, the most pronounced regional distribution gradients for the elements discussed above were observed in areas close to the southern coast. In order to get a more detailed account of the situation in this region with respect to heavy metal contamination of the natural surface soils, a new sampling campaign covering an area of about 25 000 km^2 was conducted during 1981-83. In this case, the mean distance between adjacent sampling sites was 5 km (as compared to 25 km in the 1977 national survey) and the yield was about 900 samples.

Part of this material has been analyzed with respect to Pb, Cd, and Cu (Telemark area, see Fig. 2). The maximum concentration levels for these metals in surface soil are not found along the coastline, but rather at a distance of 20-40 km from the coast, where the annual precipitation is substantially higher and the deposition of these metals is known from moss analyses to show a maximum (Hanssen et al. 1980). The close relation between variations in Pb deposition and corresponding values in surface soil is illustrated in Fig. 3. There is no apparent relationship between the zones of maximum surface soil concentrations and the occurrence of local air pollution sources such as industries and major roads.

In the coastal zone (0-60 km from the coast) of southern Norway the mean values for Pb and Cd calculated from the 1977 samples are 107 ppm and 1.1 ppm respectively. In some areas of the Telemark region receiving maximum deposition from long-range atmospheric transport due to local topographic and meteorological conditions, humus-rich soils may have levels of 200 ppm for Pb and 2.5 ppm for Cd. Similar observations were made on material recently analyzed from a region about 200 km farther west. These areas receiving especially high atmospheric inputs may warrant particular attention with respect to possible harmful effects.

SOIL PROFILE INVESTIGATIONS

Further insight into the atmospheric input to surface soils and the subsequent downward transport may be obtained from studies on soil profiles. Typical vertical distributions of Pb and Cu for soils from southern Norway and central Norway, respectively, are shown for podzol profiles in Fig. 4 and brown earth profiles in Fig. 5. The soils of southern Norway show a Pb enrichment factor of 10 or more in the surface layer relative to the underground soil, whereas no such relationship exists for the soils in central Norway where the atmospheric deposition of Pb is very low (Hanssen et al. 1980)

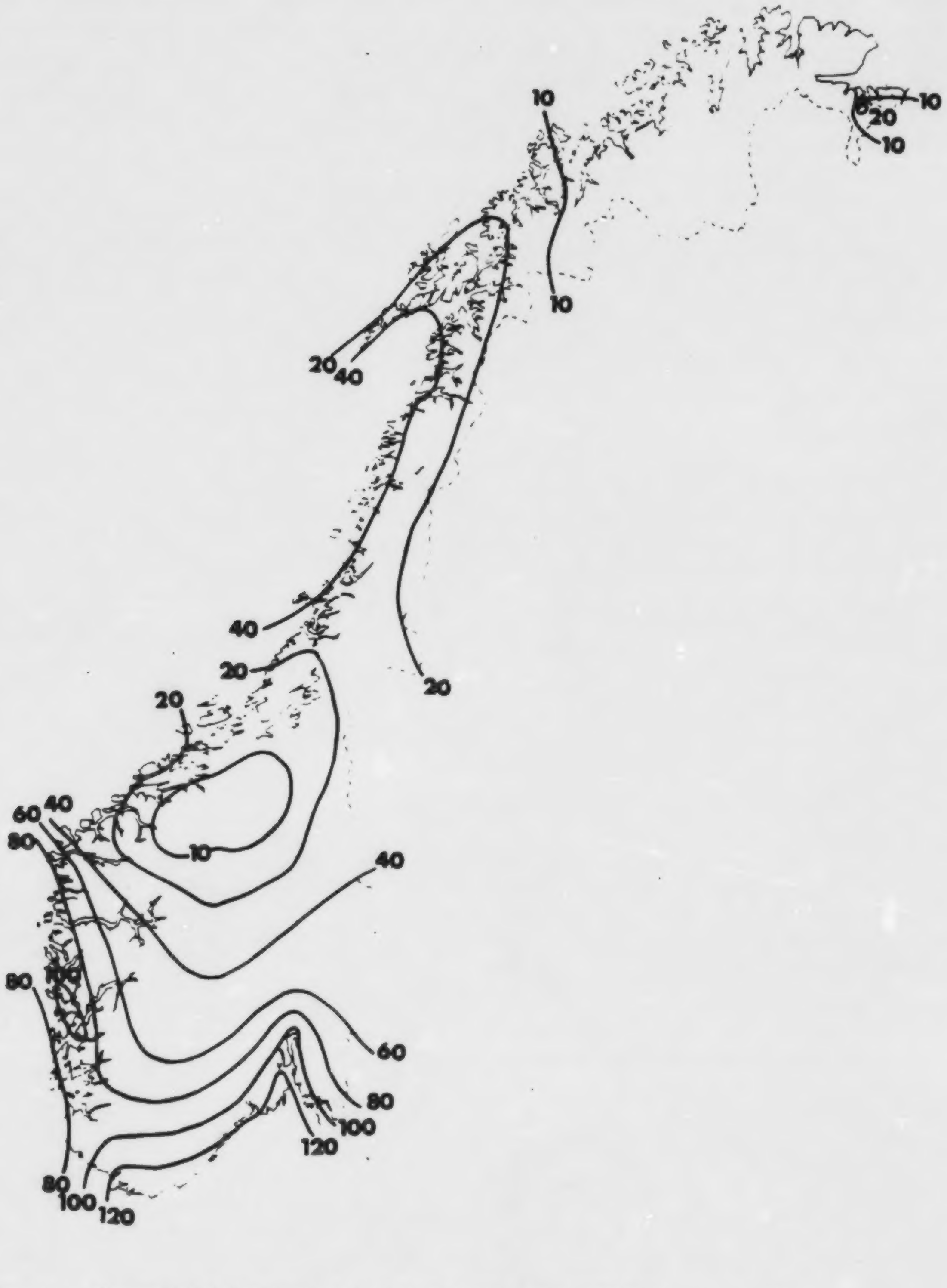
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Figure 1. Geographical distribution of lead in natural surface soils in Norway (ppm).

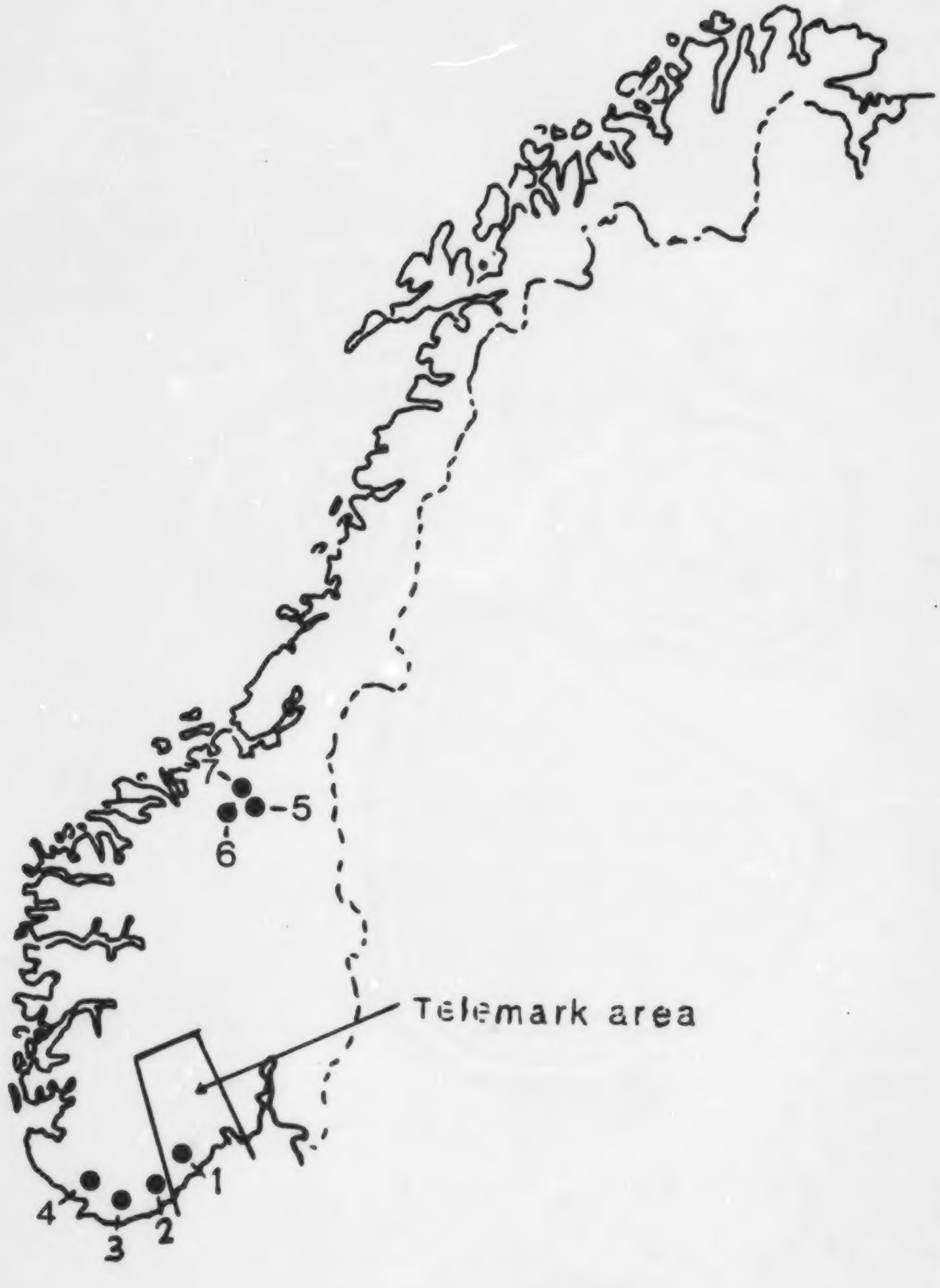
Telemark area
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Figure 2. Map showing some study areas used in this work. Locations 1-7 are the areas involved in the vegetation study.

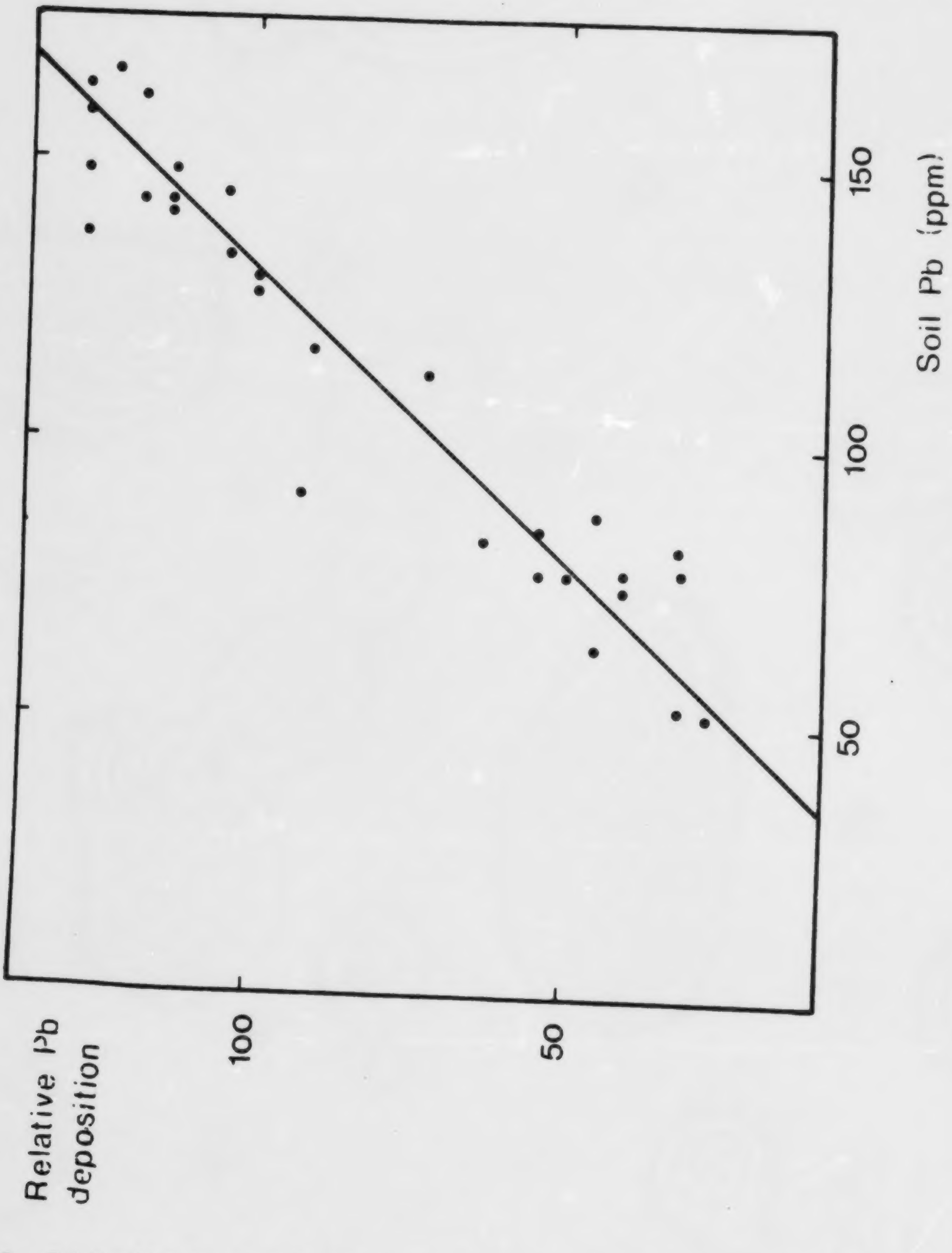

Figure 3. Relationship between soil Pb and relative Pb deposition in the Telemark area, as evident from moss analysis.

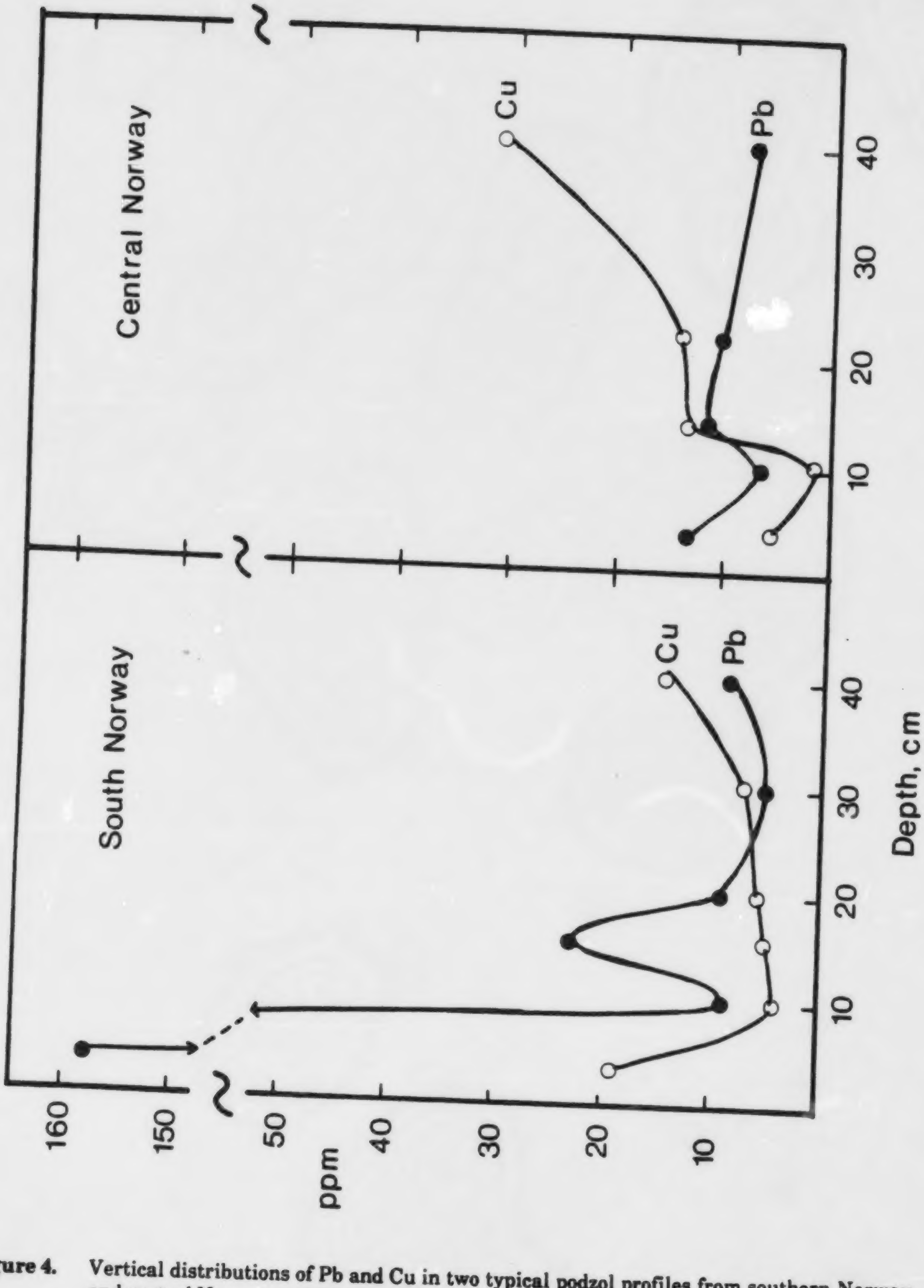

Figure 4. Vertical distributions of Pb and Cu in two typical podzol profiles from southern Norway and central Norway, respectively (ppm).

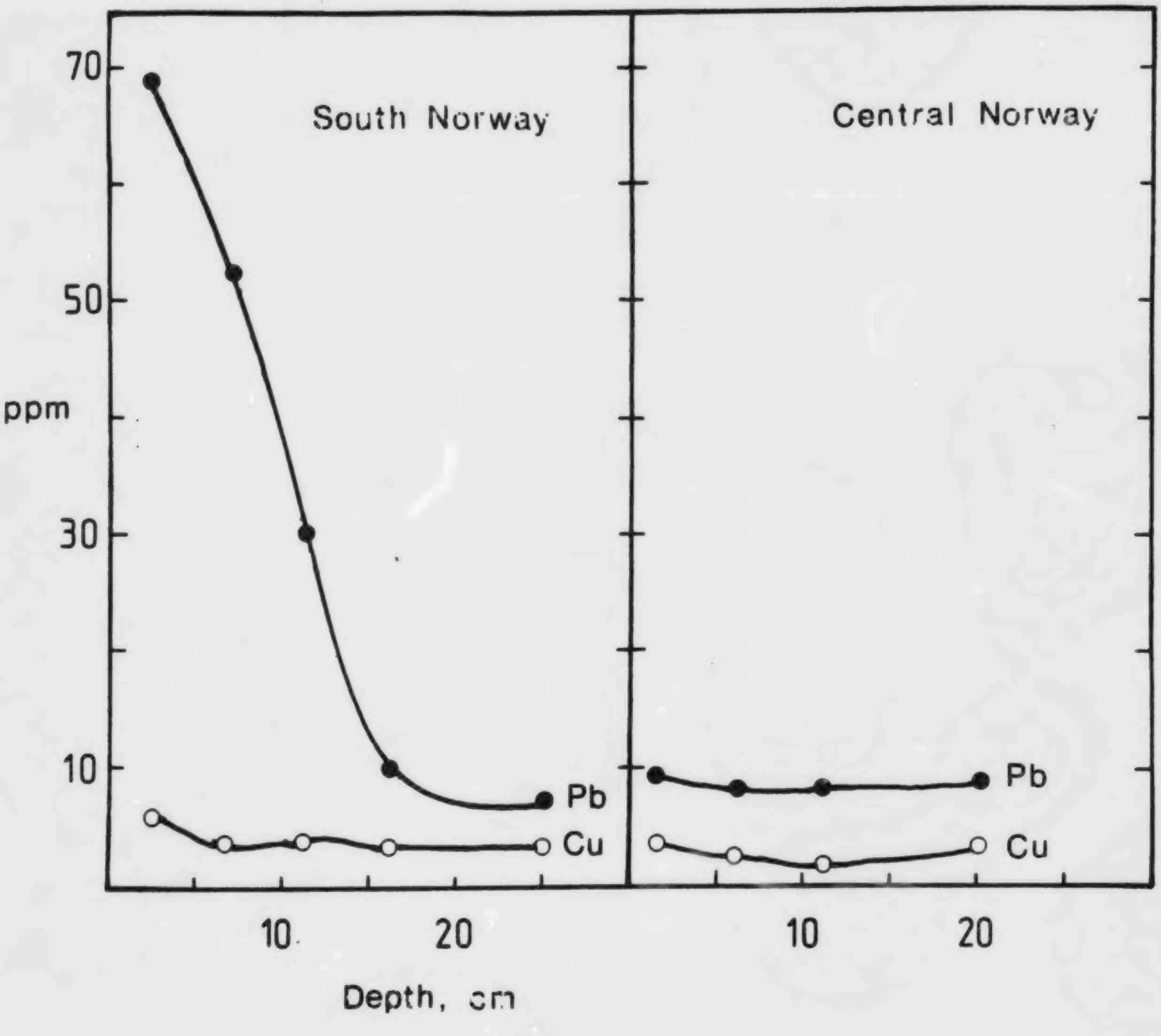

Figure 5. Vertical distributions of Pb and Cu in two typical brown earth profiles from southern Norway and central Norway, respectively (ppm).

For Cu, which is not supplied in large amounts by long-range atmospheric transport, a similar difference between geographical regions is not evident. In the case of As, another volatile trace element, the behavior in soil profiles is very similar to that of Pb (Petersen and Steinnes 1983). The detailed results from the soil profile investigations will be published elsewhere (Solberg and Steinnes, unpublished).

HEAVY METALS IN VEGETATION

Samples of higher plants (trees, heather, herbs) from seven similar coniferous forest ecosystems in southern Norway and central Norway (the locations of which are indicated in Fig. 2) were collected at three different times during the 1982 growing season. Fig. 6 shows average levels of Pb, Cd, Zn, and Cu in twigs of four common species. Concentrations of Pb and Cd are approximately 5 times higher in the samples from southern Norway than in those from central Norway. For Zn there is a slight difference in the same direction, whereas Cu does not show any significant regional difference. This is in accordance with the available information on differences in atmospheric deposition and surface soil concentrations. It is not yet clear to what extent the observed differences depend, respectively, on root uptake and foliar deposition.

CONCLUSIONS

The atmospheric supply of toxic trace elements to southern Norway, mainly from sources in other parts of Europe, leads to significantly elevated concentrations of some of these elements in surface soils and natural vegetation. Other parts of the country are less affected by long-range atmospheric transport. This situation may eventually lead to herbivorous animals in this region being significantly exposed to the elements concerned. Analysis of lamb liver samples from different parts of Norway (Frøslie et al., unpublished) revealed significantly higher concentrations of Pb and Cd in animals from southern Norway as compared to other parts of the country.

The evidence presented in this paper indicates that significant heavy metal contamination of the natural environment from atmospheric deposition may occur even at very long distances from the source region.

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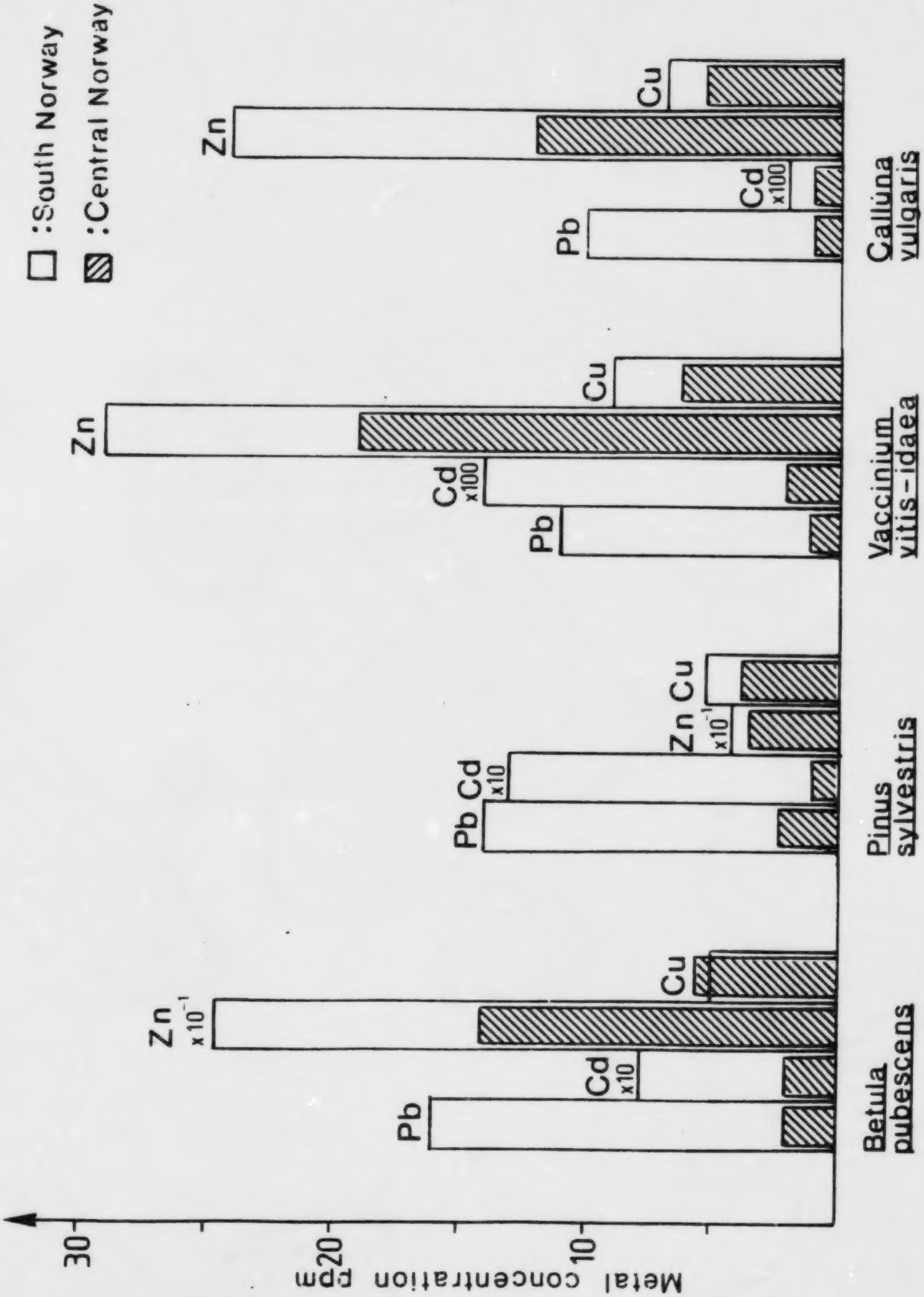

Figure 6. Mean concentrations of Pb, Cd, Zn, and Cu in samples of four common plant species from southern Norway and central Norway (ppm).

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Microbial Transformations of Sulfate in Forest Soil: Acid Rain Implications

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ABSTRACT

Sulfate is a major constituent of acid precipitation. Based on 80 gauge years of bulk precipitation chemistry measurements taken over the 2200-ha basin of Coweeta Hydrologic Laboratory in western North Carolina, SO_4^{2-} comprises 60% of the anions in precipitation. The long-term hydrologic input in bulk precipitation and export in streamflow for mixed hardwood covered watersheds shows large apparent accumulations of SO_4^{2-}, ranging from 5.9 to 8.9 kg ha^{-1} yr^{-1}. Absorption of SO_4^{2-} in the soil is a major reason for accumulation, but more recently our research has shown that metabolism of SO_4^{2-} to organic S forms by microbial populations also comprises a major pathway in the S cycle. Incubation of soils with $^{35}SO_4$ showed rapid conversion of the added SO_4^{2-} into non-salt extractable ester SO_4^{2-} and carbon-bonded S. Samples collected in August from a mixed hardwood forest showed a range in incorporation from 10.2 nmoles $^{35}SO_4^{2-}$per gram soil per 48 hours in the litter layers to 1.8 in the A horizon, 0.7 in the B horizon, and 0.2 in the C horizon. Measurements over a 10-month period showed seasonal differences with highest activities in August and September. Preliminary estimates of the potential annual flux indicate that transformations are quantitatively important in assessing the S cycle.

Microbial Incorporation of Sulfate into Organic Matter in Forest Soils

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ABSTRACT

The metabolism of inorganic sulfate into organic matter by microbial populations can be an important process in the sulfur cycle of forest ecosystems. Potential annual incorporation in forest floor and soil horizons of a mixed deciduous forest in the Southern Appalachian Mountains was estimated to be 30 kg ha^{-1}. The process is partially responsible for the apparent sulfur accumulation indicated by ecosystem budgets and affects sulfate mobility, cation leaching, and hence the interpretation of atmospheric sulfuric acid effects on forest ecosystems.

INTRODUCTION

The deposition of sulfate from acid precipitation and ocean aerosols has been identified as the major sources of the sulfate anion in forest ecosystems (Kellogg et al. 1972; Likens and Bormann 1974). However, the fate of this anion after it enters a forest ecosystem is not well known. Several studies have shown that soil sulfate adsorption can be an important component of the sulfur cycle for some forests (Johnson and Henderson 1979; Johnson et al. 1980).

Our research over the past several years suggests that microbial metabolism of sulfate to organic sulfur may also act as a major pathway in the sulfur cycle of forest ecosystems (Fitzgerald et al. 1982). The objective of this paper is to provide evidence that substantiates the quantitative importance of biological transformations of sulfate in a forest ecosystem at the Coweeta Hydrologic Laboratory in western North Carolina. Based on 10 years of bulk precipitation chemistry measurements taken over the 2185-ha basin, sulfate comprises 68% of precipitation anions. The average annual hydrologic input in bulk precipitation and export in streamflow for control, hardwood-covered watersheds during the past 10 years shows large apparent accumulations of sulfate, ranging from 5.9 to 8.9 kg ha^{-1} year^{-1} of elemental sulfur (Table 1).

STUDY SITE AND METHODS

The study was conducted on Coweeta Watershed 18, a 12.5-ha north-facing catchment which has been a primary site of long-term nutrient cycling research. Overstory vegetation on this relatively undisturbed area is dominated by *Quercus, Carya*, and *Acer* species with *Rhododendron* and *Kalmia* in the understory (Day and Monk 1977). Annual precipitation averages 180 cm and is rather evenly distributed throughout the year with at least 8 cm in most months. Catchment elevations range from 730 m to 985 m and side slopes average about 50%. Several soil types occur over the catchment but the dominant soil is a sandy loam Ashe, a member of the mesic Typic Dystrochrept family with an A_1 horizon that averages about 10 cm in thickness.

Table 1. Physical characteristics and mean annual (1973-1982) sulfate-sulfur budgets for four experimental watersheds at Coweeta Hydrologic Laboratory

Watershed number	Area (ha)	Midarea elevation (m)	Sulfate-sulfur Input	Output (kg ha^{-1} year^{-1})	Net difference
2	12.1	840	9.5	1.3	+ 8.2
18	12.5	810	10.5	1.6	+ 8.9
27	38.8	1330	13.2	7.0	+ 6.2
36	48.6	1300	11.7	5.8	+ 5.9

A permanent transect 280 m in length was established across the catchment at midelevation and traversed from ridge to stream to ridge. The transect was segmented into 10 equally spaced 0.01-ha circular plots. Three samples of the A_1 horizon were randomly collected on each plot on a monthly basis; forest floor and other soil horizons were sampled in late summer.

One gram (wet weight) of unsieved soil samples was incubated at 20°C for 48 hours with a range of 2.7 to 10.4 nmoles $Na_2\,^{35}SO_4$ (3.3×10^{10} becquerel mmole^{-1}). The incubation time was determined from a time series study of varying incubation periods which showed that $^{35}SO_4^{2-}$ incorporation into organic matter was complete after 48 hours. A range of $^{35}SO_4^{2}$ concentration was used to represent the average ambient sulfate concentrations of water in the forest floor and soil horizons. For example, the average annual sulfate concentrations of soil water collections in a mixed hardwood forest at Coweeta decreased from 105 µeq L^{-1} at 5 cm in the soil profile to 69 and 17 µeq L^{-1} at 30 and 100 cm, respectively. A more detailed description of incubation procedures can be found in Fitzgerald et al. (1982).

After incubation, the soils were washed three times with water and the solutions pooled to represent water-soluble organosulfur metabolites. Soils were then extracted three times each with 1 M Na_2SO_4, NaH_2PO_4, and LiCl and washed three times with water to yield a salt extract fraction. This procedure removes all adsorbed inorganic sulfate (Fitzgerald et al. 1982). The extracted sample was then hydrolyzed in 6 N HCl at 121°C for 12 hours; the centrifuged residue was washed with water and the sample was then held in contact with 2 N NaOH for 12 hours at room temperature and again washed with water. Acid treatment causes hydrolysis of ester sulfate (Fitzgerald 1976) and solubilization of low molecular weight fulvic acid containing carbon-bonded sulfur and sulfonate sulfur. Base treatment extracts sulfur as sulfonate and/or carbon-bonded sulfur with large molecular weight components (Fitzgerald et al. 1983). Total sulfur incorporated into organic matter was calculated as the sum of the amounts extracted by the acid and the base treatments and was termed "non-salt-extractable" organic sulfur The total extraction procedure consistently yields $\geq 90\%$ recovery of the added $^{35}SO_4^{2-}$. Soil water, salt extracts, and acid plus base fractions were analyzed by electrophoresis and radioactive components located with a scanner were determined with a scintillation counter. Complete details of laboratory methodology have been reported elsewhere (Fitzgerald et al. 1982).

RESULTS AND DISCUSSION

The influence of varying amounts of $^{35}SO_4^{2-}$ added to A_1 soil samples on quantitative recovery of the various fractions is illustrated in Fig. 1. All fractions showed a linear recovery rate over a wide range of $^{35}SO_4^{2-}$ amendments. Of the total $^{35}SO_4^{2-}$ recovered from soil samples, the water-soluble, salt-extractable, and acid plus base (non-salt-extractable) fractions consistently accounted for 50, 40, and 10%, respectively. These recoveries are similar to results previously obtained for A_1 soil samples taken from four other forest ecosystems at Coweeta (Fitzgerald et al. 1982).

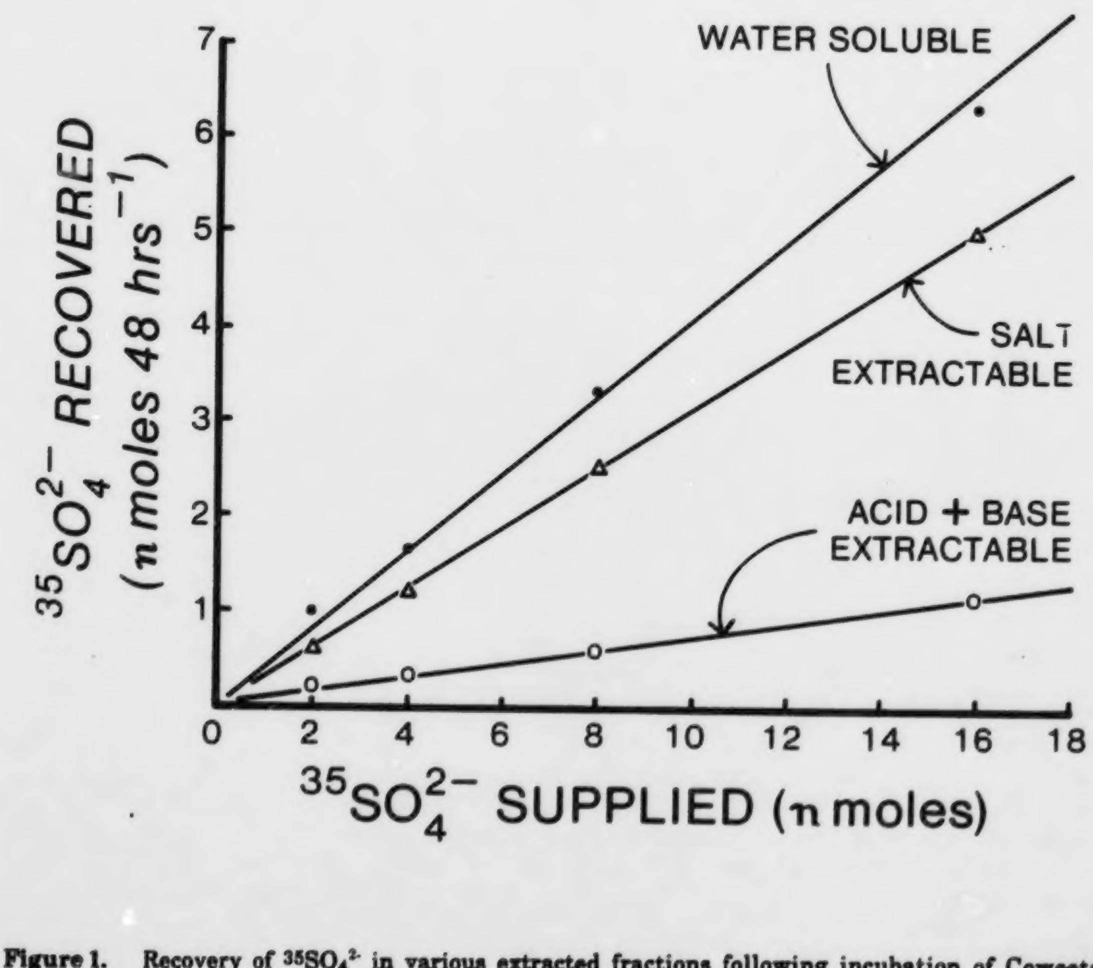

Figure 1. Recovery of $^{35}SO_4^{2-}$ in various extracted fractions following incubation of Coweeta Watershed 18 A_1 soil samples supplied with different amounts of $^{35}SO_4^{2-}$.

Additional recovery data for salt-extractable and non-salt-extractable fractions for forest floor and A_1 horizons are shown in Fig. 2. Again, recovery rates of both fractions in all horizons were a linear function of the amount of exogenous sulfate added. The O_1 and O_2 layers of the forest floor showed small but measurable quantities of adsorbed sulfate (salt-extractable fraction). The A_1 horizon is a much more active zone of adsorption, accounting for about 40% of the $^{35}SO_4^{2-}$ recovered from the samples. Significant sulfate adsorption in the A_1 horizon on Watershed 18 was also observed by Johnson et al. (1980).

In contrast to the adsorption results, $^{35}SO_4^{2-}$ incorporation activity was substantially higher in the O_1 component of the forest floor with about 55% of the added sulfate recovered in the non-salt-extractable fraction over a wide range of amended sulfate concentrations. Incorporation activity was much lower in both the O_2 and A_1 with 13 and 8% recoveries, respectively. Previous studies indicate that the non-salt-extractable fraction consists of organic matter (Fitzgerald et al. 1982; Strick et al. 1982) and that the incorporation processes are carried out by aerobically respiring organisms (Strickland and Fitzgerald 1983).

Incorporation of $^{35}SO_4^{2-}$ into organic forms of sulfur for A_1 soil horizons on Watershed 18 showed seasonal differences with highest activities occurring during August and September (Fig. 3). Lower rates of formation occurred in late spring and in winter months but samples still exhibited significant incorporation. The average activity for the year was 1.53 nmoles sulfate per gram soil per 48 hours. The potential capacity for incorporation throughout the soil profile was determined on samples collected in late August 1982 from a soil pit located at Plot 5 on the transect and for O_1 and O_2 samples collected from all 10 plots (Table 2). Concentrations of $^{35}SO_4^{2}$ added to soil samples were based on previously measured ambient sulfate concentrations because incorporation rates are concentration dependent (Fig. 2). Rates of sulfate incorporation in the O_1 and O_2 layers (Table 2) were 5 to 6 times greater than in the A_1 horizon. Incorporation rates declined rapidly in the soil profile and reached a minimum in the C horizon at a depth of 66+ cm with an activity of only 4% of that found in the surface soil.

Table 2. Formation of non-salt-extractable sulfur within the forest floor and soil horizons on Coweeta Watershed 18 in late August 1982

Forest floor and soil horizons	Depth (cm)	$^{35}SO_4^{2-}$ incorporation (nmoles per gram soil per 48 hours)
O_1	4	11.68
O_2	2	8.73
A_1	0-10	1.85
A/B	11-25	0.61
B_w	26-65	0.44
C_r	66+	0.08

A preliminary estimate of annual incorporation rates in forest floor and soil compartments can be obtained if the following assumptions are made: (1) incorporation rates generated by conditions maintained during incubation are representative of *in situ* conditions and rates, and (2) the limited data for activity rates of forest floor and remaining soil horizons are representative of transformation rates over the entire year. Annual potential incorporation of sulfate into organic matter was derived by combining activity data with prior estimates of forest floor weights and soil bulk densities (Table 3). Although high activity was observed in the forest floor, the annual potential incorporation

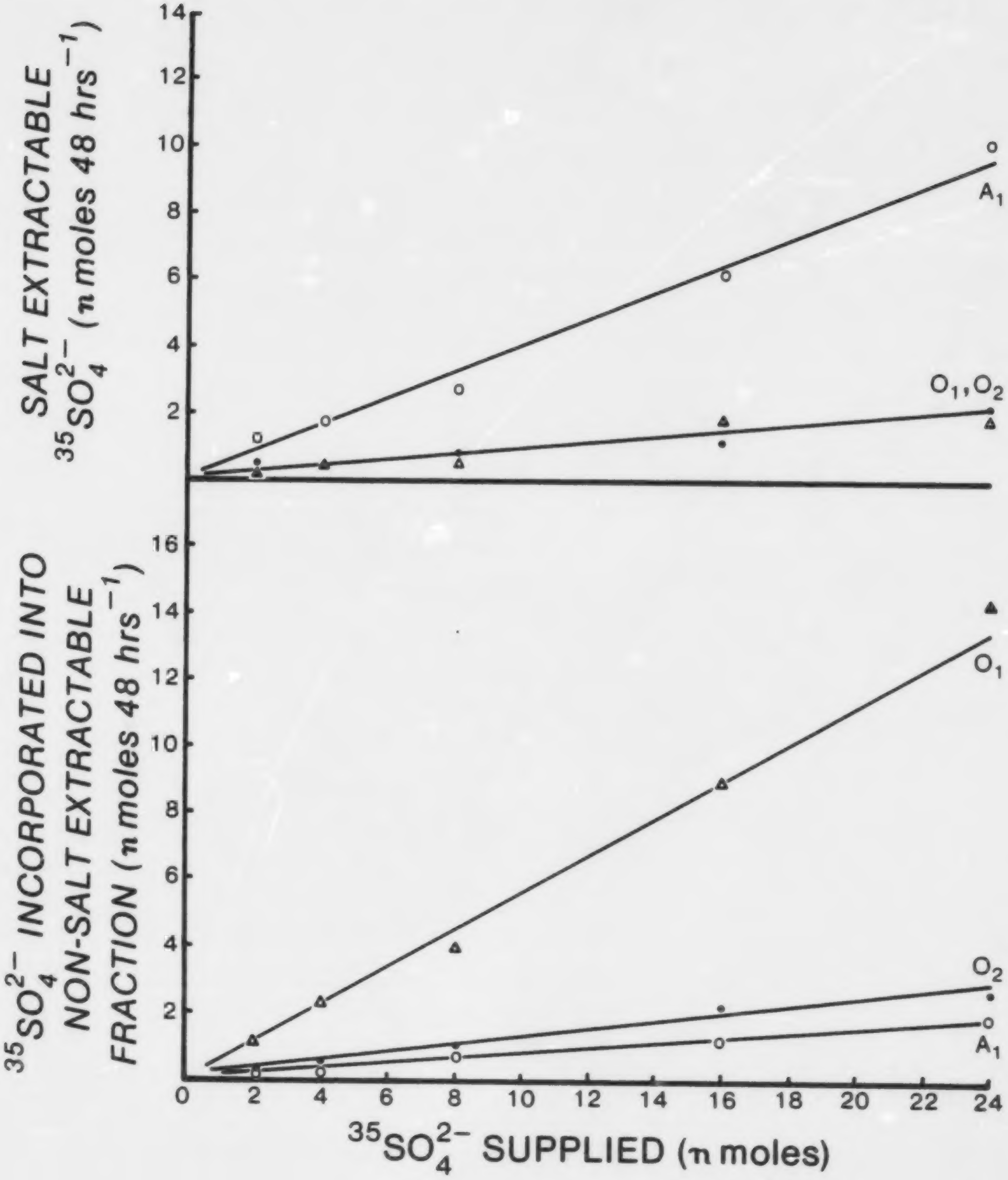

Figure 2. Recovery of $^{35}SO_4^{2-}$ in salt-extractable (top) and non-salt-extractable (bottom) fractions for O_1 and O_2 layers and A_1 soil horizon on Coweeta Watershed 18 for samples incubated with different amounts of $^{35}SO_4^{2-}$.

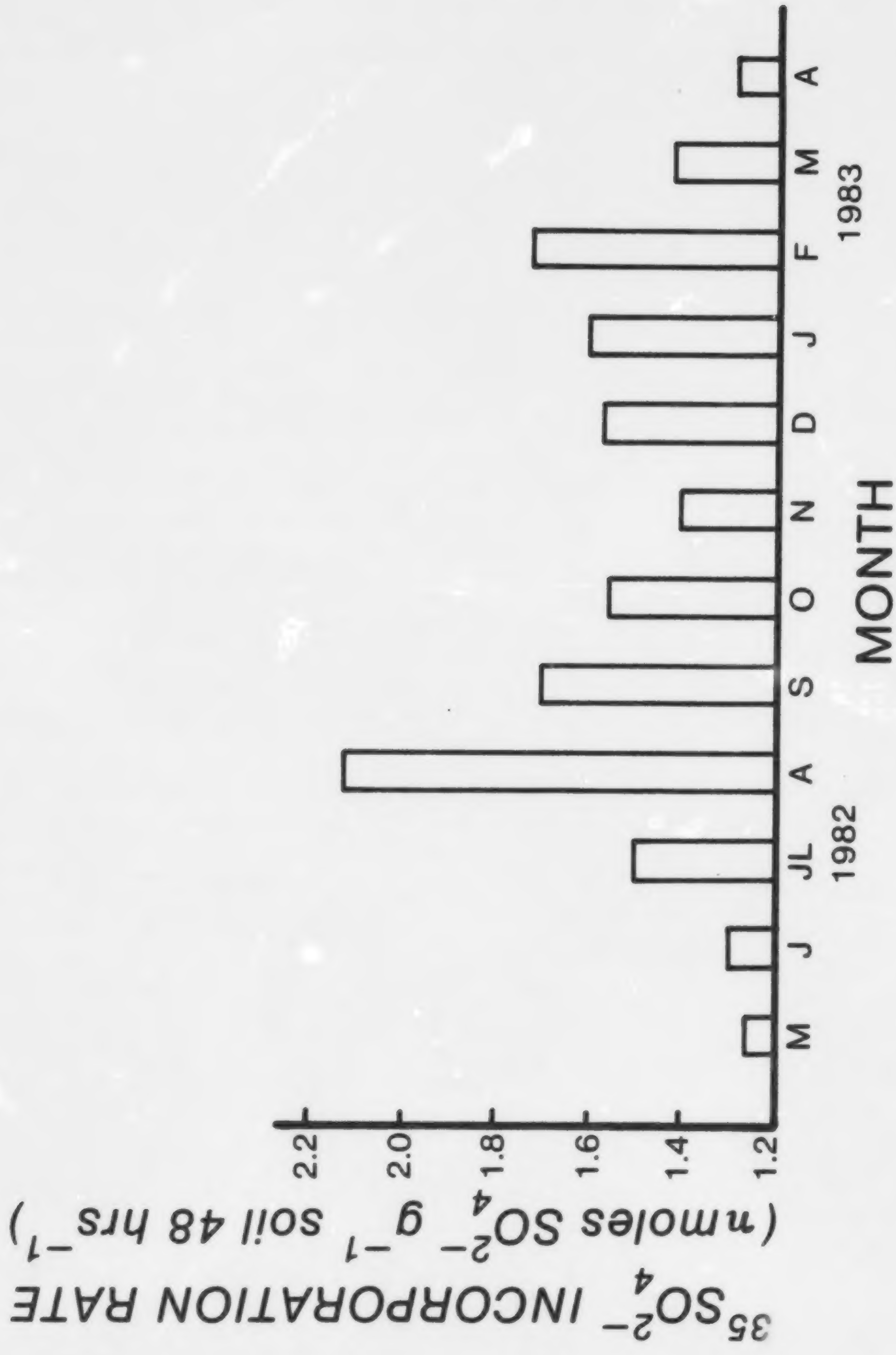

Figure 3. Monthly rates of $^{35}SO_4^{2-}$ incorporation into organic matter for A_1 soil samples from Coweeta Watershed 18. Standard error of estimates (n = 10) was ≤ ± 0.06 for most months.

of sulfur is less than 0.5 kg ha^{-1} year^{-1} because the quantity of substrate is small. In contrast, the potential flux for both the A_1 and B_w horizons is about 11 kg ha^{-1} year^{-1}. The total annual incorporation for litter and soil is 30 kg ha^{-1} year^{-1} (Table 3). These estimates represent potential rates and are probably overestimates since the activity data are based on a standard incubation temperature of 20°C. Other preliminary research conducted in our laboratory indicates that incorporation rates are lower at 5°C (Fitzgerald and Johnson 1982; Fitzgerald et al. 1983). Therefore, lower *in situ* fluxes could be expected, particularly below 10 cm in the soil profile where ambient temperatures are 5 to 10°C below the assay temperature. On the other hand, incubation conditions are representative of other *in situ* variables important in regulating sulfate incorporation such as moisture and sulfate concentrations.

Table 3. Estimates of annual potential fluxes of inorganic sulfate to organic sulfur forms by microbial populations in forest floor and soil horizons of a hardwood forest ecosystem at Coweeta Hydrologic Laboratory in North Carolina

Forest floor or soil horizon	Incorporation rate (kg sulfur ha^{-1} year^{-1})
O_1	0.2
O_2	0.2
A_1	10.7
A/B	6.1
B_w	11.1
C_r	1.5
Total	29.8

A more precise quantification of annual *in situ* incorporation will require long-term studies in all forest floor and soil horizons. The present assessment serves to place the incorporation process into perspective from an ecosystem viewpoint. The magnitude of sulfate incorporation into organic sulfur forms exceeds the bulk precipitation sulfate-sulfur input of 9 to 13 kg ha^{-1} year^{-1}. Moreover, incorporation greatly exceeds the 2 kg ha^{-1} year^{-1} of net sulfur uptake by vegetation as documented by Johnson et al. (1982) for a forest ecosystem similar to that at Coweeta. It appears that organic sulfur formation by microbial populations is a major process responsible for part of the apparent sulfur accumulation indicated by ecosystem budgets. The quantitative contribution of incorporation to apparent system accumulations of sulfur are unclear because other research we have conducted indicates that incorporated sulfur is subject to mineralization although the potential turnover rates are lower than incorporation rates (Strickland and Fitzgerald 1983; Strickland et al. 1983).

The presence of a biological pathway of sulfate transformation into organic matter has implications in the interpretation of atmospheric sulfuric acid effects on forest ecosystems. Processes which reduce the mobility of the sulfate anion also reduce cation leaching from forest soils (Johnson 1981; Lee and Weber 1982). Thus, incorporation in the forest floor and soil could provide a buffer against exogenous sulfate. Incorporation of sulfate into organic matter could also provide a soil pool of organic sulfur; if mineralization rates were accelerated, the released sulfate anion would increase cation leaching. Microbial incorporation of sulfate into organic matter, coupled with evidence for the importance of organic sulfur in forest soils (David et al. 1982) and soil sulfate adsorption, demonstrate the complexity of sulfate dynamics in the soil solution. Simultaneous examination of geochemical and biological processes is needed in a variety of forest ecosystems to more fully evaluate the source, fate, and impact of sulfate in acidification processes.

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Stratifying Wet Atmospheric Deposition Samples

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ABSTRACT

Changes in forest trees, soils, and lakes related to acid deposition cannot be ascribed to the total deposition of sulfate or nitrate and their assumed correlation with hydrogen. Of the total deposition, one portion is associated with high concentrations of salt derived from soil dust or sea spray, and another portion is associated with normally low salt concentrations and high-hydrogen concentrations. A procedure to stratify samples into one stratum dominated by basic cations (Ca, Mg, K, Na, and NH_4) and one stratum dominated by hydrogen is presented. Correlation between hydrogen and nitrate, sulfate, or the sum is dramatically improved in the H-dominated stratum. It is suggested that data in this stratum relate better to emissions and measures of resource degradation.

INTRODUCTION

Precipitation collectors sample many storm systems that pass overhead. Some storms yield precipitation with high concentrations of basic cations (Ca, Mg, K, Na, NH_4) and less hydrogen. These high concentrations originate from wind-blown soil or sea spray. Inclusion of these samples in a total data set adds considerable variation to the concentration of all ions and obscures the relation between hydrogen concentration and the concentration of nitrate or sulfate in studying acid rain. In fact, their inclusion in deposition amounts (mg m^{-2}) inflates these values by the amount of nitrate and sulfate occurring normally as metal or ammonium salts in soil minerals and sea salt. We believe the chemistry of wet atmospheric deposition samples deserves a closer look than the listing of analytical results for all samples.

Sea-derived sulfate has been routinely subtracted from total sulfate deposition in the maritime climates of northern Europe using the chloride and sulfate ratio in sea water as a tracer (Gorham 1961). However, North America is dominated by a continental climate with maritime zones narrowly restricted to its shores. Junge and Werby (1958) mapped excess sulfate (total minus sea) in precipitation over the United States, but the map showed greater excess sulfate inland than near the shores indicating the land surface as a major source of sulfate. We developed a method to stratify precipitation samples into those dominated by high concentrations of basic cations regardless of their source (soil or sea), and those that span a range from normal to emission-laden. We labelled the latter stratum hydrogen-dominated, though this is not always true.

This paper introduces a simple method to stratify wet deposition samples into two strata. The reasons for doing this are those normally advocated in statistical texts: (1) to provide an estimate of a mean closer to the true population mean, and (2) to reduce the amount of variation about the estimate of the mean. This argument can logically be extended to linear regression analyses, and it is here that sample stratification can clarify interpretation and provide a certainty not possible when total data sets are used. Within a given data set, the precision of testing correlation between hydrogen and anions is improved even though sample numbers are reduced. A rigorous discussion of the stratification method is not developed here, but its usefulness in identifying correlates of hydrogen in precipitation is illustrated. First the stratification method is presented, then an analysis of hydrogen-anion correlation (linear regression) is performed on the hydrogen-dominated stratum for data at the Marcell Experimental Forest in north central Minnesota and the Wellston Field Laboratory in west central Michigan (near Cadillac). Data from both locations are from samples collected over a one-week period and analyzed according to the National Atmospheric Deposition Program (NADP) protocol. Both sampling sites are located in forest openings in predominately forested regions.

METHODS

Precipitation samples can be stratified solely on the magnitude of cations. This avoids bias that might occur if the acid rain anions of nitrate and sulfate were considered. Cations are plotted on rectangular coordinates with the microequivalent per liter (μeq L^{-1}) sum of basic cations (Ca, Mg, K, Na, NH_4) on the X axis and the acidic cation hydrogen (H) on the Y axis (Fig. 1). Any sample falling above a 1:1 line is thus dominated by H, whereas any sample falling to the right is dominated by basic cations.

Within the basic cation stratum it is easy to understand that samples with high concentrations can be dominated by soil dust or sea spray, and within the H-dominated stratum it is defined that samples with high concentrations are acid. However, samples near the origin are not very acid and it is reasonable to assume that the region near the origin represents normal conditions for low concentrations in either stratum. To allow for normal variation near the origin we offset the diagonal 1:1 line to the right by an X-intercept equal to 50 μeq L^{-1} of basic cations. This was done on the basis of the highly skewed frequency distribution of basic cations measured on the Marcell Experimental Forest. At low concentrations, the frequency plot exhibits a mode of 25 μeq L^{-1}. Beyond two modes (50 μeq L^{-1}) the distribution is strongly skewed to the right reflecting the influence of soil dust (Fig. 1).

The stratification method was applied to 179 precipitation samples at Marcell, MN, and to 157 samples at Wellston, MI, from July 1978, through all of 1982, and March 1979, through all of 1982, respectively. At Marcell, 73 samples, or 41%, fell in the basic cation stratum; at Wellston, 41 samples, or 26%, fell in this stratum.

Linear regression analyses (units in μeq L^{-1}) were performed for H against nitrate, H against sulfate, and H against nitrate plus sulfate, for samples in the H-dominated stratum and the total data set. The reduction in the residual mean square from the total data set to the H-dominated data set was calculated as a percent to indicate the effectiveness of stratifying. Finally, the amount of wet deposition in the total and H-dominated data sets was calculated to show the portion of each major ion associated with hydrogen.

RESULTS AND DISCUSSION

There were no significant correlations between hydrogen and nitrate, sulfate, or nitrate plus sulfate, at the Marcell site when total data sets were used. In the H-dominated data set, nitrate was significantly (alpha = 0.05) correlated with hydrogen, and the reduction in residual mean square from the total to H-dominated stratum was 40% (Fig. 2). Even in the H- dominated data set, sulfate was not correlated with hydrogen at Marcell, but the nitrate correlation was strong enough to give a significant correlation between hydrogen and nitrate plus sulfate (Table 1). An earlier attempt at sample stratification at the Marcell site showed similar results and that a mean sulfate concentration of 1.8 mg L^{-1} should be considered a normal background value (Verry 1983).

At Wellston, MI, linear regressions between hydrogen and nitrate, sulfate, or their sum were significant in both the total and H-dominated data sets. However, the regressions in the H-dominated set had residual mean squares that were 16, 68, and 76% less than in the total sets for nitrate, sulfate, and their sum respectively (Table 1). The nitrate plus sulfate scatter plots at Wellston are shown in Figure 3.

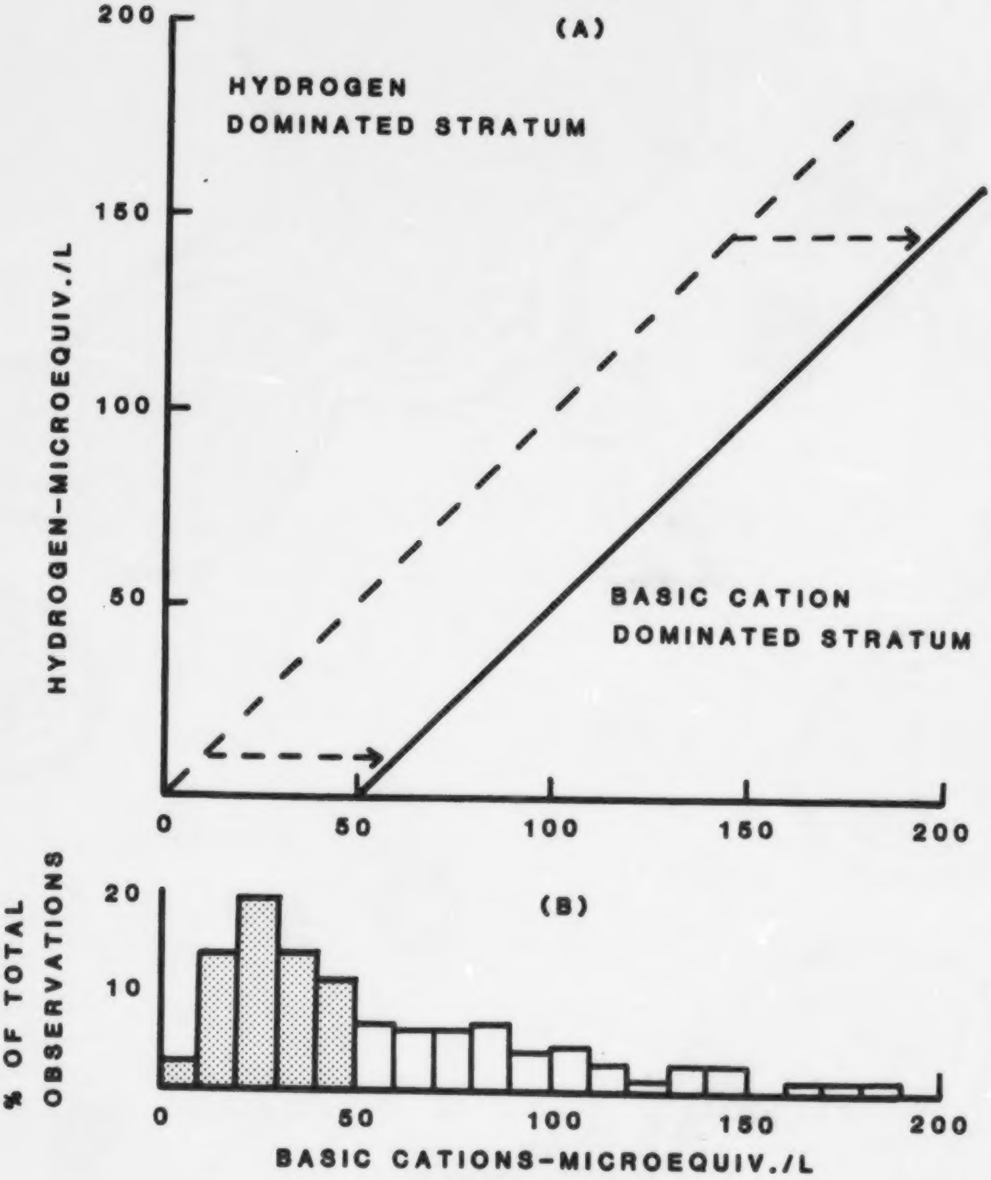

Figure 1. A method (A) to stratify wet atmospheric deposition samples into those dominated by basic cations (Ca, Mg, K, Na, NH_4) and those dominated by hydrogen. The X-intercept (A) has been moved 50 μ L^{-1} to the right to allow for normal variation (shaded) found in the sum of basic cations (B).

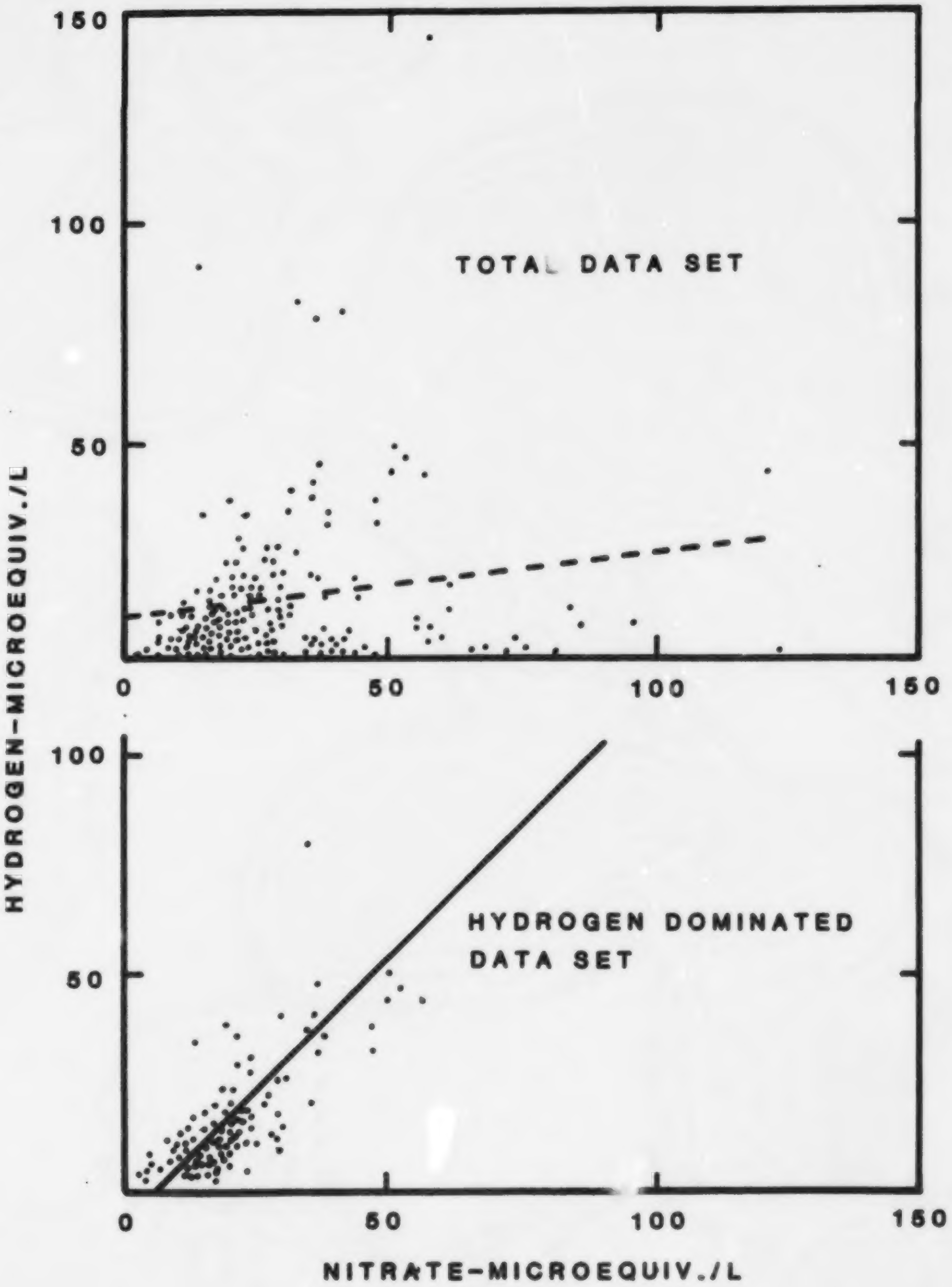

Figure 2. The relationship between hydrogen and nitrate in total and hydrogen dominated data sets at Marcell, Minnesota, for July 1978 through 1982. Some dots represent several samples. The dashed line is not a significant regression (alpha = 0.05).

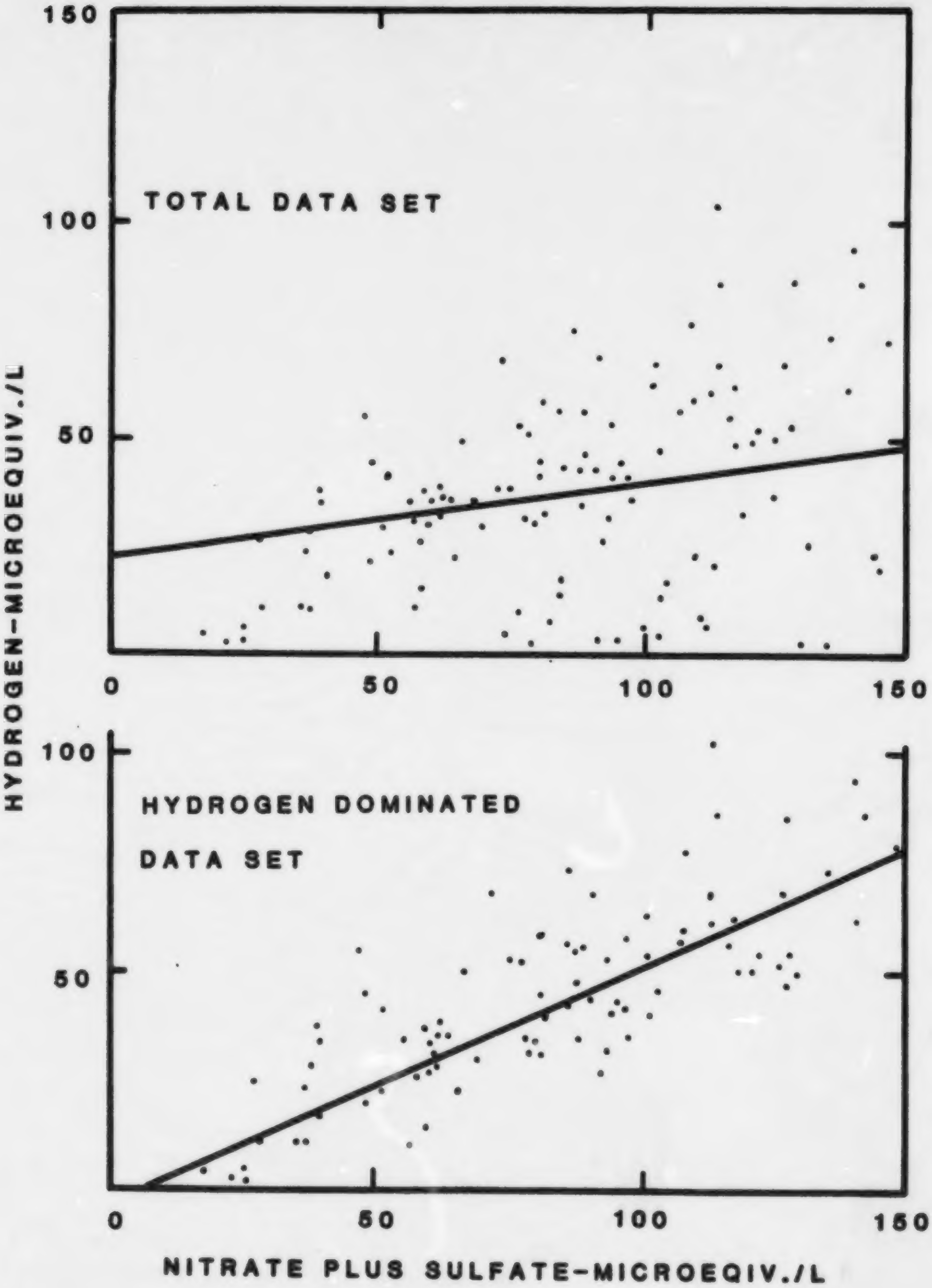

Figure 3. The relationship between hydrogen and nitrate plus sulfate in total and hydrogen-dominated data sets at Wellston, Michigan, for March 1979 through 1982. Some dots represent several samples. Plotting was truncated at 150.

Table 1. Mean concentration and hydrogen regression data for NADP samples at Marcell, Minnesota, and Wellston, Michigan, 1978-1982

	Total data set		H-dominated data set	
Means and regression parameters	Marcell MN	Wellston MI	Marcell MN	Wellston MI
Means	μeq L^{-1}			
H	11.84	42.77	16.10	51.33
NO_3	27.62	44.46	19.47	37.88
SO_4	41.43	75.85	23.97	62.83
NO_3 & NO_4	69.10	120.31	43.44	100.71
(No. samples)	(179)	(157)	(106)	(116)
Linear regression				
	Hydrogen over nitrate			
r^2	0.01	0.18	0.52	0.55
intercept	9.72	21.42	-7.86	9.50
slope	0.08	0.48*	1.23*	1.10*
resid. mean square	304	935	182	462
(% reduction)			(40)	(51)
	Hydrogen over sulfate			
r^2	0.00	0.18	0.07	0.70
intercept	12.91	24.74	7.08	6.93
slope	-0.03	0.24*	0.38	0.71*
resid. mean square	307	936	347	303
(% reduction)			(-13)	(68)
	Hydrogen over nitrate plus sulfate			
r^2	0.00	0.20	0.31	0.79
intercept	11.56	21.39	-5.86	-1.86
slope	0.00	0.18*	0.51*	0.53*
resid. mean square	308	911	258	216
(% reduction)			(16)	(76)

* A significant regression with a slope different from 0 at alpha = 0.05.

An important observation of the scatter plots in Figure 3 is that the variance for the total data set is not equally distributed. Thus, correlation between hydrogen and nitrate plus sulfate (and separately) is done in violation of basic statistical assumptions and with a lot of variability. On the other hand, the variance in the H-dominated regression is equally distributed and has 76% less variation than the total data set.

Table 2. Wet deposition at Marcell, Minnesota, and Wellston, Michigan, for total and hydrogen-dominated data sets, 1979-1982

Data set	Ca	Mg	K	Na	NH_4	NO_3	Cl	SO_4	PO_4	H	Precip.
	(mg m^{-2} or kg ha^{-1} x 100) yr^{-1}										cm
Marcell, Minnesota											
Total	253	48	48	180	327	1098	120	1355	6.6	10.2	87.4
H-dominated	112	24	21	57	177	684	64	788	2.0	9.3	64.2
% of total	44	50	43	32	54	62	54	58	30.0	91.0	73.0
Wellston, Michigan											
Total	339	93	45	302	427	2223	288	3056	43.0	43.2	98.5
H-dominated	208	55	28	146	307	1639	208	2268	40.0	39.7	78.5
% of total	61	59	62	48	73	74	72	74	92.0	92.0	81.0

The deposition of each major ion in both the total and H-dominated data sets is given for both sites in Table 2. Note that the H-dominated strata retained over 90% of the total hydrogen deposited in precipitation. All other ions have a lower percentage in the H-dominated stratum at Marcell, MN, than at Wellston, MI, where the mean hydrogen concentration in the total data set is four times greater.

Application of a stratification procedure to wet deposition samples does not account for dry deposition; however, Ulrich (1980) concludes that dry deposition (based on tree interception studies) includes the same ions in the same ratio as wet deposition. Thus, we can use wet deposition as an index of the relation between hydrogen and various anions and extend stratification methods to dry deposition when interpretable collection procedures are developed.

We believe that the stratification procedure described above will help to describe acidic deposition with a precision not attainable in total data sets. It needs testing in areas where sea salt can dominate some samples, and it needs application to all of North America. Although we examined regressions between hydrogen and nitrate or sulfate, regressions in the H-dominated set can also include chloride where emissions from the burning of high-chloride coal exist. In these situations, the stratification should separate samples high in NaCl from those high in HCl.

CONCLUSIONS

We believe that the chemistry of wet atmospheric deposition samples deserves a closer look than the listing of analytical results for all samples. These samples should be stratified into a set dominated by basic cations and a set dominated by hydrogen. It is in the H-dominated set that we find statistically viable relationships between hydrogen and the anions of nitrate, sulfate, and chloride. Mapping these relationships will or will not show where specific anions correlate with hydrogen in a fashion yielding much greater certainty in prediction than total data sets can supply. Precise relationships should guide legislative proposals for emission control and will serve best to test the effectiveness of control efforts.

ACKNOWLEDGMENTS

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GLOSSARY OF TERMS

Vegetation

To assist in the identification of the principal woody species making up the composition of different regions of Canada and the United States, reference may be made to Rowe (1972) and Anon. (1980).

For the botanical equivalents of common names used by various authors, the following table, taken from Rowe (1972), should assist.

Alder	*Alnus* spp.
Alder, red	*Alnus rubra* Bong. (*Alnus oregona* Nutt.)
Arbutus	*Arbutus menziesii* Pursh
Ash, black	*Fraxinus nigra* Marsh.
Ash, blue	*Fraxinus quadrangulata* Michx.
Ash, green	*Fraxinus pennsylvanica* Marsh. var. *subintegerrima* (Vahl) Fern.
Ash, red	*Fraxinus pennsylvanica* Marsh.
Ash, white	*Fraxinus americana* L.
Aspen, largetooth	*Populus grandidentata* Michx.
Aspen, trembling	*Populus tremuloides* Michx.
Basswood	*Tilia americana* L.
Beech	*Fagus grandifolia* Ehrh.
Birch, Alaska	*Betula neoalaskana* Sarg.
Birch, dwarf	*Betula glandulosa* Michx.
Birch, grey	*Betula populifolia* Marsh.
Birch, Kenai	*Betula papyrifera* Marsh. var. *kenaica* (W.H. Evans) Henry
Birch, northwestern white	*Betula papyrifera* Marsh. var. *subcordata* (Rydb.) Sarg.
Birch, yellow	*Betula alleghaniensis* Britton (*Betula lutea* Michx. f.)
Birch, western white	*Betula papyrifera* Marsh. var. *commutata* (Reg.) Fern.
Birch, white	*Betula papyrifera* Marsh.
Blue-beech	*Carpinus caroliniana* Walt.
Butternut	*Juglans cinerea* L.
Cascara	*Rhamnus purshiana* DC.
Cedar, eastern red	*Juniperus virginiana* L.
Cedar, eastern white	*Thuja occidentalis* L.
Cedar, western red	*Thuja plicata* Donn
Cherry, black	*Prunus serotina* Ehrh.
Chestnut	*Castanea dentata* (Marsh.) Borkh.
Cottonwood, black	*Populus trichocarpa* Torr. & Gray
Cottonwood, eastern	*Populus deltoides* Bartr.
Cucumber-tree	*Magnolia acuminata* L.
Cypress, yellow	*Chamaecyparis nootkatensis* (D. Don) Spach

Douglas-fir, coast	*Pseudotsuga menziesii* (Mirb.) Franco
Douglas-fir, interior (blue)	*Pseudotsuga menziesii* (Mirb.) Franco var. *glauca* (Beissn.) Franco
Elm, rock	*Ulmus thomasii* Sarg.
Elm, slippery	*Ulmus rubra* Mühl.
Elm, white	*Ulmus americana* L.
Fir, alpine	*Abies lasiocarpa* (Hook.) Nutt.
Fir, amabilis	*Abies amabilis* (Dougl.) Forbes
Fir, balsam	*Abies balsamea* (L.) Mill.
Fir, grand	*Abies grandis* (Dougl.) Lindl.
Gum, black	*Nyssa sylvatica* Marsh.
Hackberry	*Celtis occidentalis* L.
Hazel	*Corylus cornuta* Marsh.
Hemlock, eastern	*Tsuga canadensis* (L.) Carr.
Hemlock, mountain	*Tsuga mertensiana* (Bong.) Carr.
Hemlock, western	*Tsuga heterophylla* (Raf.) Sarg.
Hickory, butternut	*Carya cordiformis* (Wang.) K. Koch
Hickory, mockernut	*Carya tomentosa* Nutt.
Hickory, pignut	*Carya glabra* (Mill.) Sweet
Hickory, shagbark	*Carya ovata* (Mill.) K. Koch
Hop-hornbeam	*Ostrya virginiana* (Mill.) K. Koch
Juniper, Rocky Mountain	*Juniperus scopulorum* Sarg.
Kentucky Coffee-tree	*Gymnocladus dioicus* (L.) K. Koch
Larch, alpine	*Larix lyallii* Parl.
Larch, western	*Larix occidentalis* Nutt.
Maple, bigleaf	*Acer macrophyllum* Pursh
Maple, black	*Acer nigrum* Michx. f.
Maple, Manitoba	*Acer negundo* L.
Maple, mountain	*Acer spicatum* Lam.
Maple, red	*Acer rubrum* L.
Maple, silver	*Acer saccharinum* L.
Maple, sugar	*Acer saccharum* Marsh.
Mountain-ash, showy	*Sorbus decora* (Sarg.) Schneid.
Mulberry, red	*Morus rubra* L.
Oak, black	*Quercus velutina* Lam.
Oak, bur	*Quercus macrocarpa* Michx.
Oak, chestnut	*Quercus prinus* L.
Oak, chinquapin	*Quercus muehlenbergii* Engelm.
Oak, Garry	*Quercus garryana* Dougl.
Oak, pin	*Quercus palustris* Muenchh.
Oak, red	*Quercus rubra* L.
Oak, scarlet	*Quercus ellipsoidalis* E.J. Hill
Oak, swamp white	*Quercus bicolor* Willd.
Oak, white	*Quercus alba* L.

Pawpaw	*Asimina triloba* (L.) Dunal
Pine, eastern white	*Pinus strobus* L.
Pine, jack	*Pinus banksiana* Lamb. (*Pinus divaricata* (Ait.) Dumont)
Pine, limber	*Pinus flexilis* James
Pine, lodgepole	*Pinus contorta* Dougl. var. *latifolia* Engelm.
Pine, pitch	*Pinus rigida* Mill.
Pine, ponderosa	*Pinus ponderosa* Laws.
Pine, red	*Pinus resinosa* Ait.
Pine, shore	*Pinus contorta* Dougl. var. *contorta*
Pine, western white	*Pinus monticola* Dougl.
Pine, whitebark	*Pinus albicaulis* Engelm.
Poplar, balsam	*Populus balsamifera* L.
Sassafras	*Sassafras albidum* (Nutt.) Nees
Spruce, black	*Picea mariana* (Mill.) B.S.P.
Spruce, Engelmann	*Picea engelmannii* Parry
Spruce, Porsild	*Picea glauca* (Moench) Voss var. *porsildii* Raup
Spruce, red	*Picea rubens* Sarg.
Spruce, Sitka	*Picea sitchensis* (Bong.) Carr.
Spruce, western white	*Picea glauca* (Moench) Voss var. *albertiana* (S. Brown) Sarg.
Spruce, white	*Picea glauca* (Moench) Voss
Sycamore	*Platanus occidentalis* L.
Tamarack	*Larix laricina* (Du Roi) K. Koch
Tulip-tree	*Liriodendron tulipifera* L.
Walnut, black	*Juglans nigra* L.
Willow	*Salix* spp.
Yew, western	*Taxus brevifolia* Nutt.

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Soils

To assist in the identification of the principal soil groups and associations mentioned by authors from Canada, the United States and other countries, the following table of equivalents has been prepared. Further details may be found in Clayton et al. (1977) and Anon. (1978). The World terms are those of FAO/UNESCO, as used in the "Soil Map of the World".

Canadian	United States	World
Podzolic	Spodosol	Podzol
	Some Inceptisols	
Luvisol	Hapludalf or Glossudalf	Luvisolic
Gray		Albic
Brunisolic	Inceptisol, some Psamments	Cambisol
Melanic or Eutric Brunisol	Eutrochrept	Eutric
Sombric or Dystric Brunisol	Umbric Dystrochrept	Dystric
Organic	Histosol	Histosol
Crysolic	Pergelic Subgroups	Gelic
Dystric	Dystro	Dystric
Podzolic	Haplorthod	Podzols, Leptic
Luvisolic	Boralf & Udalf	Luvisol
"	Fragiudalf Hapludalf	Orthic
"	Ultisol	Acrisol
"	Hapludalt	Orthic
"	Ochraquult	Gleyic
		Plinthic

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